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THE UNIVERSITY OF ALBERTA

"HIGH VISCOSITY CRUDE OIL DISPLACEMENT IN A.

LONG UNCONSOLIDATED NATURAL SAND PACK USING CARBONATED BRINE"

BY

M. FAZIL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE

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IN PETROLEUM ENGINEERING

FACULTY OF ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "High Viscosity Crude Oil Displacement In a Long Unconsolidated Sand Pack Using Carbonated Brine" submitted by Mohammad Fazil in partial fulfillment of the requirements for the degree of Master of Science.



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Acknowledgment is also made to the Research Council of Alberta, The California Standard Oil Company and the oil industry for the financial support of the research project in which the author was engaged.

ABSTRACT

A series of brine flood tests were made on a long unconsolidated sand pack to evaluate the effect of carbon dioxide as an additive to the displacing fluid. Natural brine, natural sand and heavy crude oil from the Lloydminster area were used.

Carbonated brine flooding showed significant increases in oil production over conventional water flood. The increase in recovery of oil is attributed to a decrease in viscosity and interfacial tension, and a volume expansion of oil when contacted by carbonated brine.

The sand pack was found to be slightly oilwet or neutral but successive carbonated floods seemed to change it to a preferentially water wet system.



INTRODUCTION

This study was undertaken to determine if water flooding with carbonated brine would increase the recovery of heavy crude oil over conventional brine flood recoveries. This work is a part and a continuation of a larger research project concerned with recovery of heavy crude oil. In order to simulate reservoir conditions, natural sand and fluids were used in this study.

Primary recovery of heavy crude oil reservoirs has been very low.

Reservoir stratification and in particular unfavourable mobility ratios suggest that secondary recovery projects may not be successful.

Carbonated water flooding is an improved method of secondary recovery.

A certain amount of carbon dioxide is dissolved in water at selected temperatures and pressures. This carbonated water is then used to displace oil from the reservoir rock. A number of investigators have studied the process of carbonated water flooding in the laboratory and in the field. Laboratory and field tests with carbonated water have shown increases in recovery of oil.

Martin (1) indicated that carbon dioxide with or without adjuvant when dissolved in flood water increased the recovery of oil both in field and laboratory tests. The increase in oil production was attributed to certain properties of carbon dioxide.

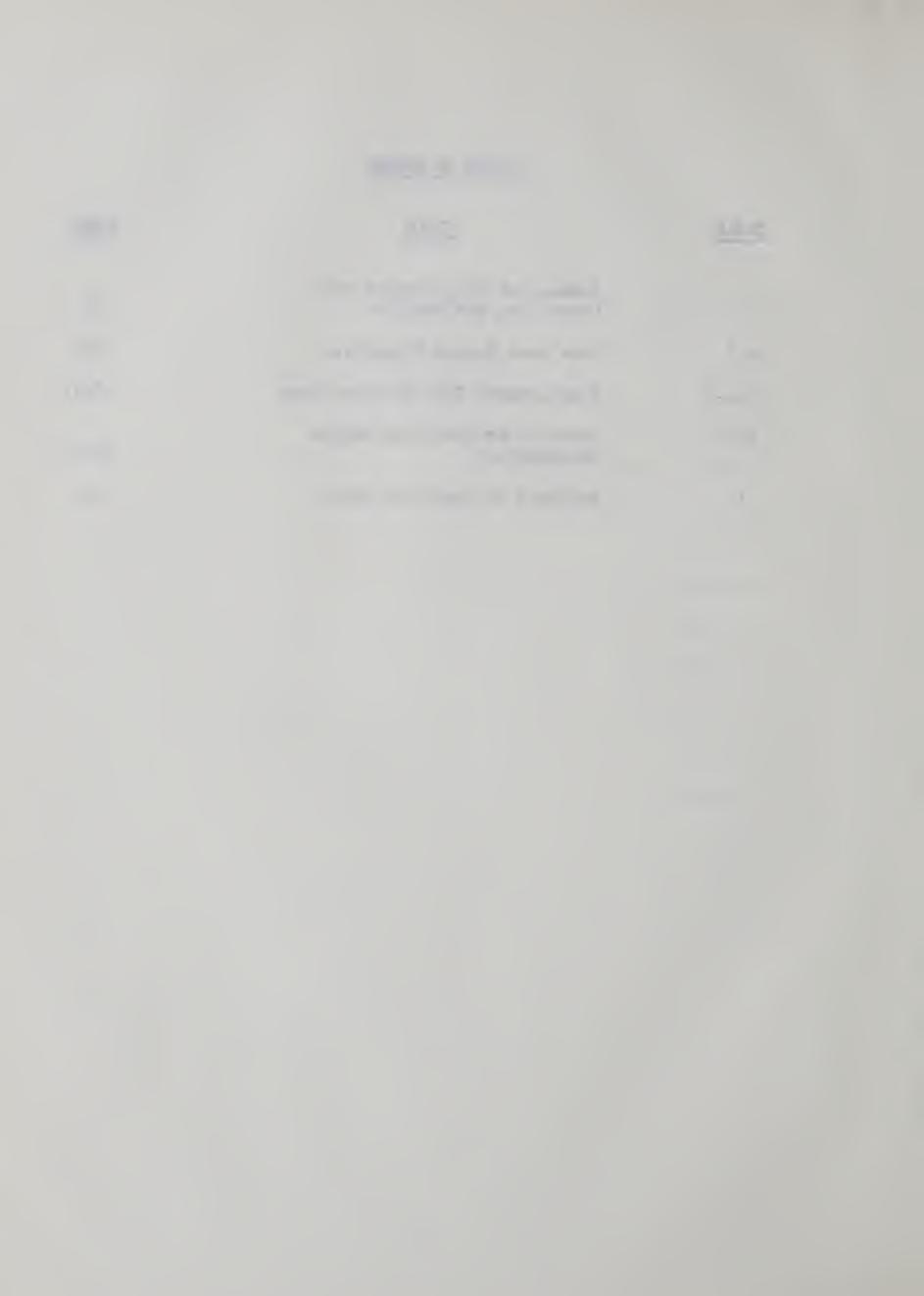
- 1) It is highly soluble in oil. It swells the oil and reduces its viscosity. It is completely miscible with the lighter portion of a crude oil.
- 2) It is highly soluble in water. When dissolved in water it chemically reacts with certain portions of the reservoir rock.

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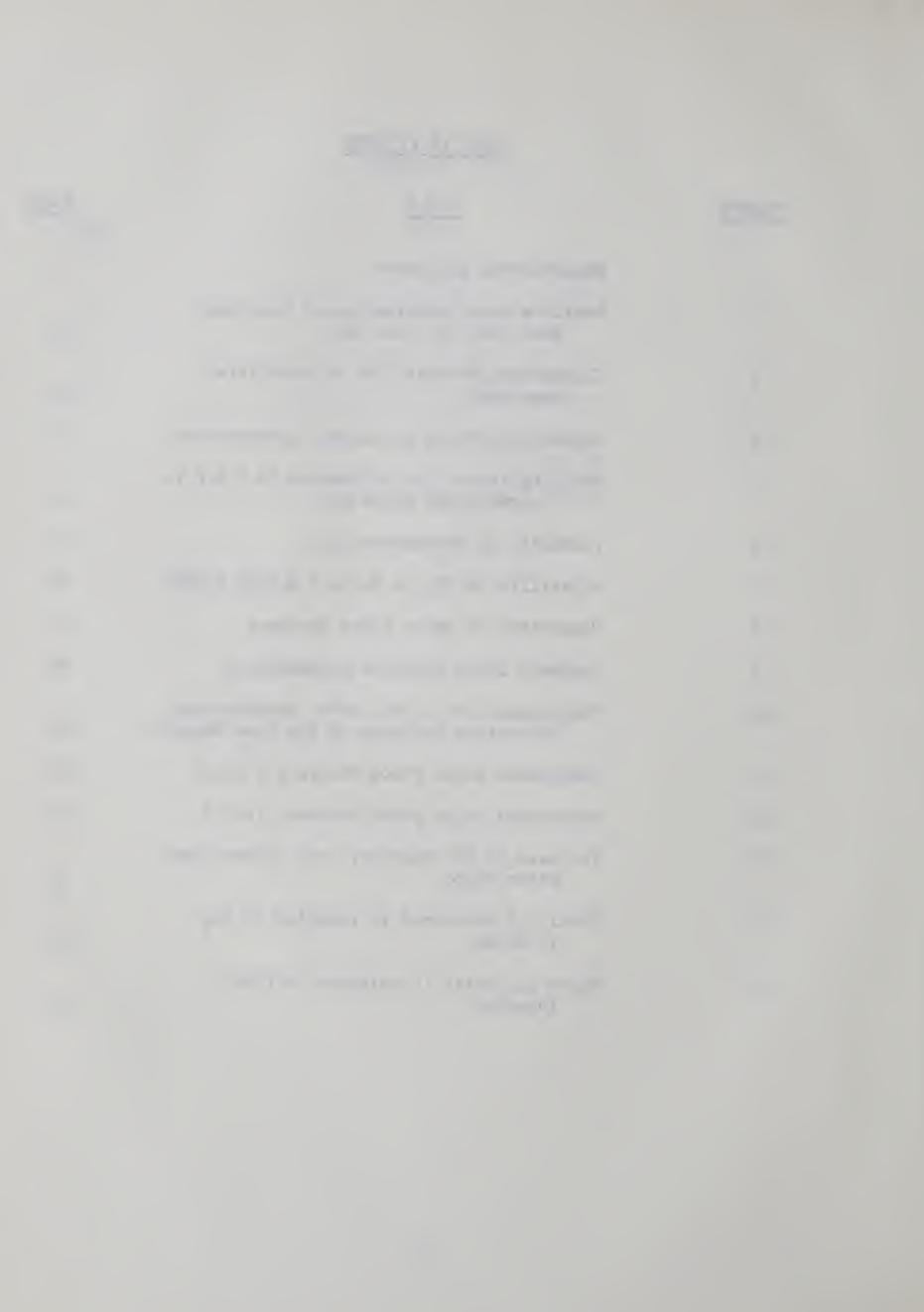
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INTRODUCTION

This study was undertaken to determine if water flooding with carbonated brine would increase the recovery of heavy crude oil over conventional brine flood recoveries. This work is a part and a continuation of a larger research project concerned with recovery of heavy crude oil. In order to simulate reservoir conditions, natural sand and fluids were used in this study.

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Reservoir stratification and in particular unfavourable mobility ratios suggest that secondary recovery projects may not be successful.

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Martin (1) indicated that carbon dioxide with or without adjuvant when dissolved in flood water increased the recovery of oil both in field and laboratory tests. The increase in oil production was attributed to certain properties of carbon dioxide.

- 1) It is highly soluble in oil. It swells the oil and reduces its viscosity. It is completely miscible with the lighter portion of a crude oil.
- 2) It is highly soluble in water. When dissolved in water it chemically reacts with certain portions of the reservoir rock.
- 3) It is extremely compressible under certain conditions. Its critical temperature is about 89°F.

LITERATURE REVIEW

The use of carbon dioxide to recover oil from underground reservoirs is not a new subject. About the time of the first World War the Soda Water System was devised and on December 4, 1917, Patent No. 1239,232 was issued to Frederick Squires (2). The method involved injecting carbonated water through an input well and recovering the oil through a producing well. The carbonated water could be prepared by dissolving the carbon dioxide in water either at the surface or at the bottom of the well bore.

In early 1940, Martin observed chemical reactions between dry ice and lubricating oil. This led him to experiment with the use of carbon dioxide for the recovery of oil from underground reservoirs. During subsequent laboratory and field work, several other observations associated with carbonated water injection were made. It was found that carbonated water promoted the solution of salts such as calcium and magnesium carbonates.

$$H_2O + CO_2$$
 H_2CO_3 $MgCO_3 + H_2CO_3$ $Mg(HCO_3)_2$ $Ca(HCO_3)_2$

The bicarbonates of calcium and magnesium are soluble. This increased the permeability in the carbonate rocks and also the rocks having calcium and magnesium carbonates as the cementing material. The presence of carbonated water retards the swelling of montmorillonite clays if present in the rocks. The carbon dioxide when dissolved in water forms carbonic acid and thus depresses the hydroxyl ions present in the pure water. These hydroxyl ions if present enter into the lattice structure of the clay and bring about its swelling.

Jhonson et al (3) noted a considerable increase in oil recovery when using carbonated water. The increase oil recovery was obtained from fresh as well as resaturated samples of Bradford and Richbury sand. Additional oil

recovery was obtained even after the samples were previously flooded with brine. The authors suggested that there was a possibility that carbonated water reacted with adsorbed or bonded semi-organic films on the mineral surfaces of sand pores, and released them and any oil which might be attached thereto. It was further suggested that these adsorbed films were the reason for the so-called oil wet sands.

Other authors (4,5) observed a higher recovery of oil with carbonated water as compared to conventional water flood. The increased oil production was found to be a function of carbon dioxide concentration in the displacing fluid. The additional oil production was attributed to the properties of the water/oil system in the presence of carbon dioxide, namely reduction in oil viscosity, oil volume expansion, decrease in the oil water interfacial tension and the effect on the rock wettability.

Holm (17) observed that oil recovery obtained in the long narrow model (length/width = 6) was considerably higher than that for models with lower length/width ratios. X-ray shadowgraphs taken during the floods also showed that very little fingering took place in the narrow models and that a high percentage of the model was contacted during the flood.

The presence of carbon dioxide in the injection fluid minimized viscous fingering. As carbon dioxide, from the displacing fluid diffused into the oil, the viscosity and interfacial tension of oil and water was decreased whereas the mobility and overall conformance of the flooding process were improved. The diffusion rates of carbon dioxide into oil were quite high which tended to minimize fingering and overriding effects.

EXPERIMENTAL EQUIPMENT

Displacement Tests

The core holder consisted of a high pressure stainless steel pipe suitable for an unconsolidated sand pack. The end plates, also of stainless steel, were fitted with brass insert lining. A stainless steel screen of 200 mesh was placed between the sand and the end plates which were grooved concentrically and radially to facilitate flow. The core holder was 122 centimeters long with an inside diameter of 5 centimeters.

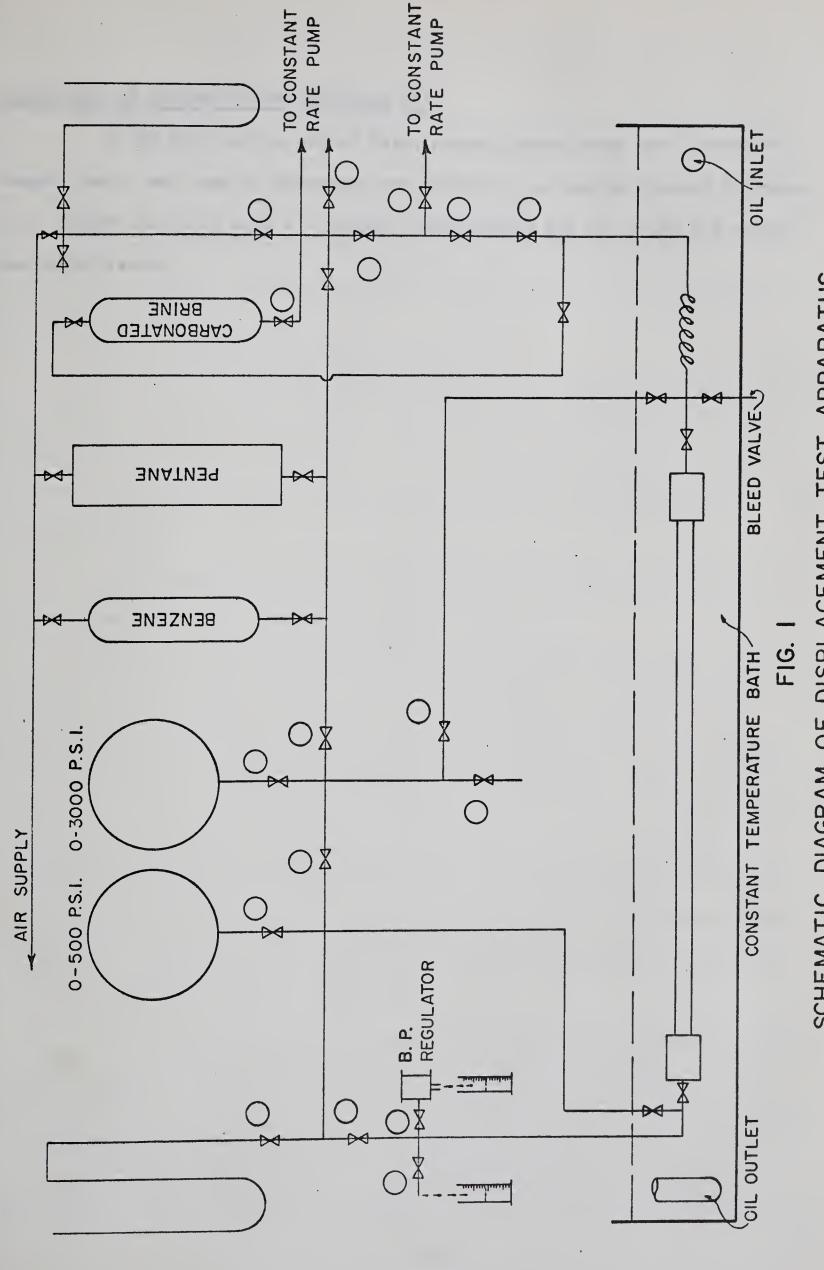
The end plates were fitted with valves on both sides and pressure taps connected to two Heise gauges with ranges of 0-500 psi and 0-3000 psi. The two pressure gauges were interconnected so that any one could be used for recording upstream and downstream pressures. The downstream end was fitted with a back pressure gauge connected to a nitrogen bottle. The core assembly was set inside a retangular metallic oil bath. Oil was circulated continuously with a pump and the temperature was controlled within $^{\pm}1^{\circ}F$.

A model 2249WII double barrel constant rate Ruska pump was used for all tests. Two stainless steel bombs of about three litres capacity were used to hold carbonated water and benzene. A plastic cylinder contained pentane which was used to clean the core. Collecting graduated cylinders were kept in a high temperature bath. The cylinders were connected to the constant rate pump shown by the arrows on the right of Fig. 1.

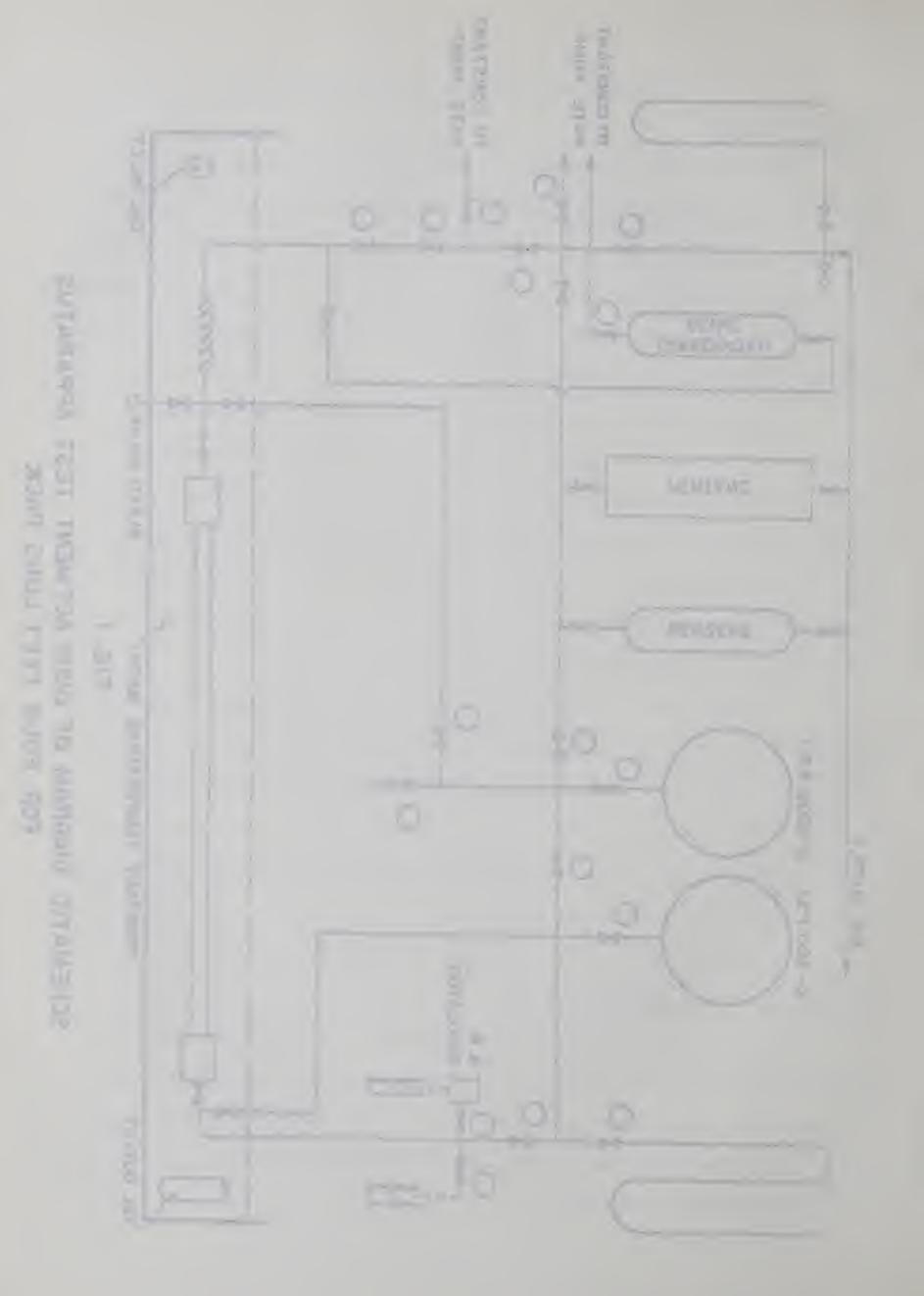
A complete sketch of the equipment is shown in Fig. 1.

Solubility of Carbon Dioxide in Brine

The solubility of carbon dioxide in brine was determined using a Jerguson cell mounted on a stand with a provision so that it could be rocked back and forth. The cell was connected to a pressure gauge and carbon dioxide bottle. A wet test meter was used to measure the amount of carbon dioxide dissolved in brine at different pressures.



SCHEMATIC DIAGRAM OF DISPI ACFMENT TEST APPARATUS FOR FOUR FEET LONG PACK



Solubility of Carbon Dioxide in Crude Oil

A PVT cell with a set of Heise gauges, Ruska pumps and a stand for sample bombs, was used to determine the solubility of carbon dioxide in crude oil. Based upon this data a viscosity relationship for the crude oil system was established.



EXPERIMENTAL PROCEDURE

Natural Sparky sand from Fargo Husky Lone Rock A-7-9-47-27 well was used for the artificial core pack. Sand from the rubber sleeve core was mixed up thoroughly and cleaned with benzene until all traces of staining were removed. After evaporating the benzene the sand was dried in the oven at 250°F. During cleaning of sand some finer particles may have been lost. A sieve analysis of the sand was also run.

Natural brine from the Lloydminster area was used for all the displacement tests. For carbonated floods, the natural brine was saturated with carbon
dioxide gas at different pressures. The formation water was filtered and stored
in a glass container. If the water contained rust, it was filtered again before
using for any test.

Lloydminster crude oil was used for all the tests. This 16.0° API gravity cleaned crude oil contained 0.2% B.S. & W.

The core holder was hand packed with dry clean Sparky sand. A copper tube with one inch diameter cap at one end was used for tamping the sand. A gas permeability test was run on the dry core, using clean, dry air and nitrogen. Permeability was determined using Klinkerberg's method (6). After evacuating, the core was saturated with brine to find its pore volume and porosity. The brine permeability was determined using Darcy's law for linear incompressible fluid flow. Brine saturated core was flooded with oil to an irreducible water saturation. A material balance maintained on the core system determined the saturations of oil and water at any time.

The effluent water and oil during a displacement test were emulsified. It was therefore, necessary to heat the contents of the graduated cylinders in a temperature bath, in spite of the addition of emulsion breaking compounds.

The first displacement test was run using only the natural brine.
This formed the basic data for comparing recoveries of oil by carbonated water

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floods to those from conventional water floods. Four more displacements tests were run using brine, saturated with carbon dioxide at different pressures. About two pore volumes of carbonated brine were used. This was followed by two more pore volumes of brine to flush out all the carbon dioxide from the core before starting a new flood. The fluids in the core were considered free of carbon dioxide when no effervescence was noticed from the effluents. This procedure was repeated for the four carbonated brine floods.

To find the solubility of carbon dioxide in brine a Jerguson cell with a capacity of 198 c.c. was used. This cell was connected to a pressure gauge and the carbon dioxide source. The measurements were taken at room temperature (78°F). The cell was filled with 150 millilitres of brine and carbon dioxide was passed into it. The cell was rocked back and forth to give better and faster dissolution of gas in the fluid. The pressure was recorded and the carbon dioxide source was cut off. The pressure dropped as more carbon dioxide dissolved in the brine. After a certain time there was no further drop in pressure. This pressure was taken as the saturation pressure of the sample.

The volume of carbon dioxide in the cell and that coming out of solution was measured with a wet test meter. Knowing the total volume of carbon dioxide and the volume occupied by the free carbon dioxide in the cell, the solubility in SCF/BBL was calculated. The solubility of carbon dioxide at room conditions was determined by the titration method and was added to the calculated solubility at the particular pressure and temperature.

The solubility of carbon dioxide in crude oil was determined by using a PVT cell. Six bombs were filled with 50 c.c. of crude oil each. Different amounts of carbon dioxide were injected into the bombs. The pressure of all these bombs was raised to about 1800 psia by injecting mercury. These were left for a considerable time so that all the carbon dioxide would be dissolved in the oil.

About 25 c.c. of the carbonated oil sample was transferred to the PVT cell and the relationship of pressure and volume was noted. The saturation pressure of the sample was determined by plotting pressure vs volume of mercury injected.

A stainless steel bomb with a capacity of 3215 c.c. was filled with 3000 c.c. of brine. The fluid was de-aerated and connected to a carbon dioxide supply. This bomb was also mounted in a fixture so that it could be rocked back and forth so as to give a faster saturation of brine with carbon dioxide. The pressure of the system was recorded after the carbon dioxide supply was cut off. As more carbon dioxide went into the solution there was a drop in pressure of the system. After a certain period there was no further pressure drop and this was considered to be the saturation pressure for the sample. Free carbon dioxide from the bomb was displaced into a small cylinder pressured up with mercury. While transferring free carbon dioxide the pressure of the system was kept a few pounds above the saturation pressure so that carbon dioxide did not escape from the solution. This carbon dioxide saturated brine was then used for the carbonated brine floods.

MODEL SCALING

The nature of multiphase flow through porous media is such that the respective geometrics of a laboratory model and of the field critically effect the relationship of the rates observed in the laboratory or the field. For a meaningful projection of results from laboratory observations to an expected behavior on field scales, special care must be exercised in selecting the geometry and physical parameters of the system to be investigated in the laboratory.

Leverett (7) first utilized the concept of dimensional groups to scale laboratory experiments involving immiscible flow displacements. Rapoport (8) used the concept of inspectional analysis. Geertsma (9) and Perkins (10) extended the scale up laws given by Rapoport and Croes and Schwarz (11), and others (12,13) experimentally verified them. The form of scaling co-efficient used by Rapoport, was (LVUw).

It was found that for low values of the scaling co-efficient the recovery was effected by the capillary forces. However, after a critical value of scaling co-efficient break-through recovery was not reduced by the capillary forces. de Haan (14) expanded the capillary scaling number, I for a completely water wet system by considering interfacial tension and permeability.

$$I = \frac{LV / Uw}{\sqrt{K}}$$

where L = length of the model

V = superficial velocity

Mw = viscosity of water

O = interfacial tension

K = permeability

In the present work, sand, crude oil and brine, all from an actual field were used during the displacement test. Viscosity, density, capillary pressure, interfacial tension, contact angle would therefore present no problem.

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The length to diameter ratio of the model was 24.4. The rate of displacement was selected considering the capillary effects.

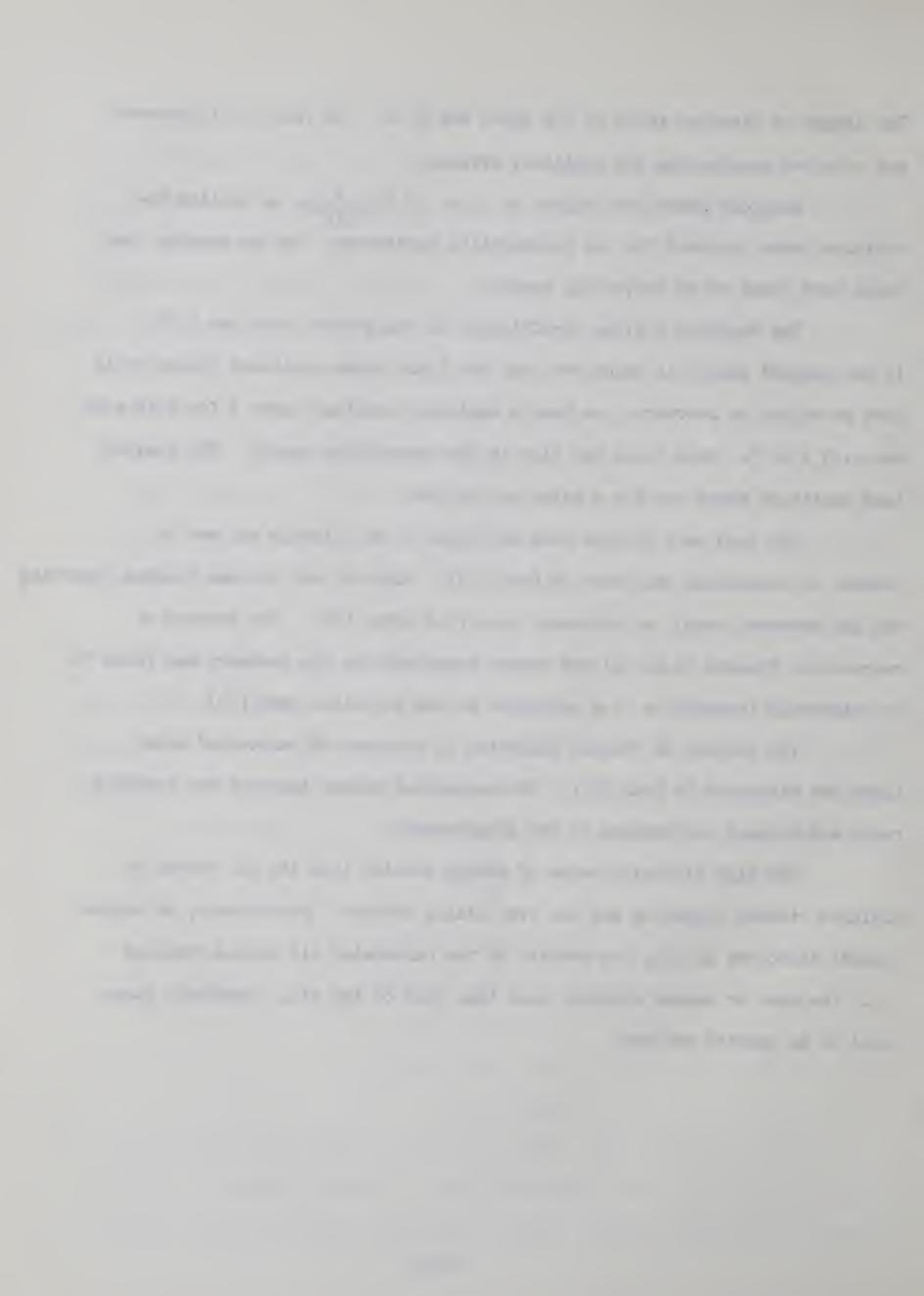
Rapoport found that values of 0.4 - 0.8 cm. 2 cps. as scaling coefficient were critical for low permeability sandstones. Values greater than these were found to be adequately scaled.

The Rapoport scaling co-efficient in the present work was 1.03. It was decided that this value was near the limit where capillary forces would have no effect on recovery. de Haan's capillary scaling number I for this work was 1.15×10^{-1} . This value was also in the insensitive region. The scaling laws mentioned above are for a water wet system.

The sand pack in this work was found to be slightly oil wet or neutral by comparison with work of Fatt (15). With oil wet systems viscous fingering was not observed until at extremely high flow rates (16). The absence of macroscopic fingers in an oil wet system explained why the recovery was found to be relatively insensitive to a variation in the injection rate (14).

The subject of viscous fingering in the case of carbonated water flood was discussed by Holm (17). The carbonated system improved the mobility ratio and overall conformance of the displacement.

The high diffusion rates of carbon dioxide into the oil tended to minimize viscous fingering and the over riding effects. Furthermore, as carbon cloxide dissolved in oil, the density of the carbonated oil system remained to the same or became slightly less than that of the oil, therefore, there would be no gravity effects.



EXPERIMENTAL RESULTS AND DISCUSSION Properties of the Core System

A sample of the natural sand used for the core pack was passed through a sieve and the result is shown in Fig. 2, Table A-1. A plot of grain size distribution showed the major portion of the total particles to be of fine grain size. About 8% of total particles were -200 mesh which were of extremely fine grain referred to as silt.

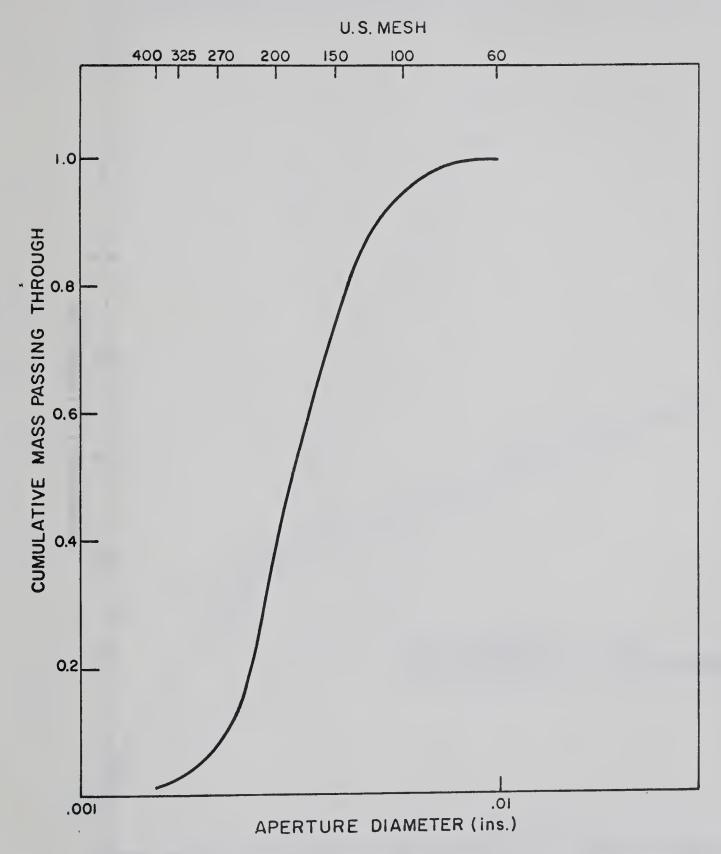
Air permeability was established by Klinkenberg's method (6) at 2.32 Darcies as shown in Fig. 3. Brine permeability was established at 2.035 Darcies after flooding the core for a few hours. Collins (18) and Scott (19) noted a decrease in permeability if the core was left in contact with brine for an extended period. This was explained as due to the swelling of clay in the sand pack. However, in the present study there was no appreciable change in permeability during a three hour period.

Properties of Carbon Dioxide

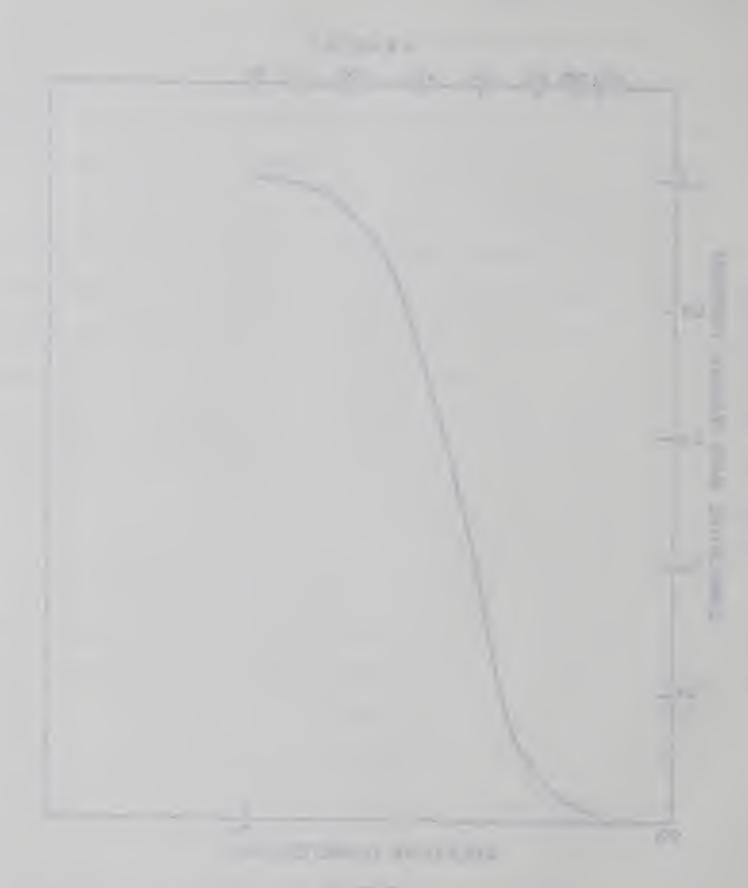
Fig. 4 presents data of this work and from literature (20,21) which shows an increase in solubility of carbon dioxide in hydrocarbons (SCF/BBL) as a function of pressure. The solubility increased with an increase in pressure in all cases. It also showed that solubility also increased with an increase in A.P.I. gravity of crude oil. Welker (21) showed that solubility of carbon dioxide in oils decreased with increasing temperatures and the formation volume factor indicated a corresponding drop, both of which were the usual behaviour for the solubility of gases in liquids. Carbon dioxide became completely miscible with lighter hydrocarbons (4) in the pressure range of 800-1000 psi.

Volume Expansion of Crude Oil

Fig. 5 presents the calculated swelling factor for the Lloydminster crude oil. The volume expansion of oil was calculated using the empirical formula given by Welker (21).



PARTICLE SIZE DISTRIBUTION
OF LONE ROCK SAND USED FOR CORE PACKING



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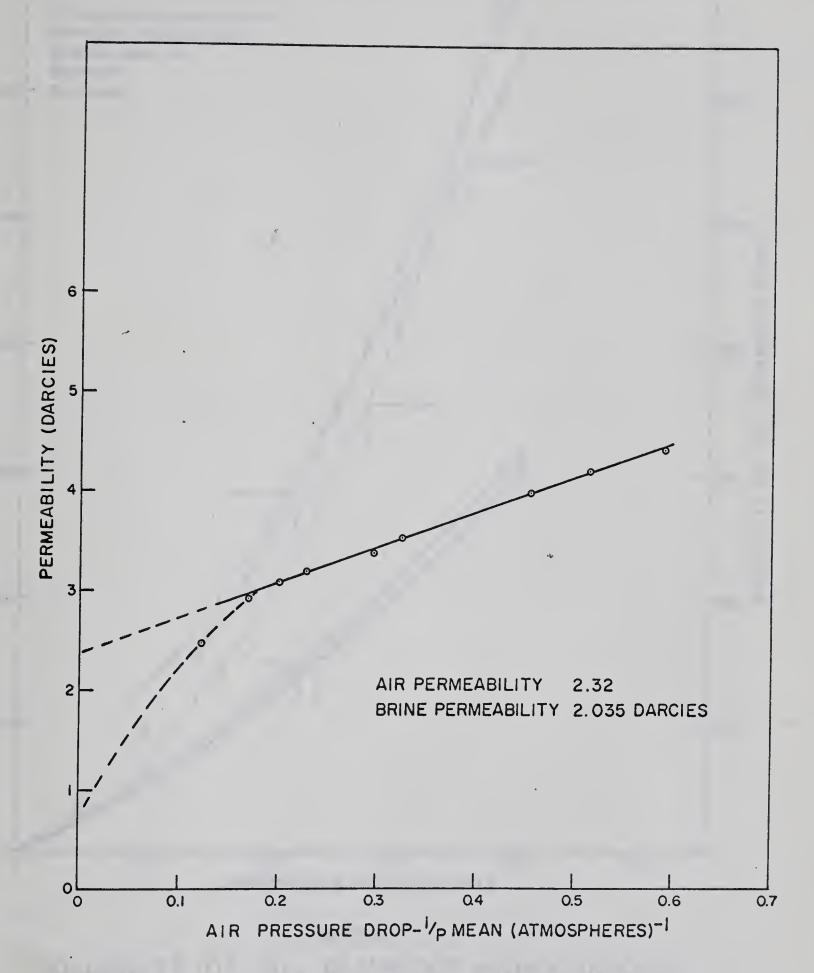
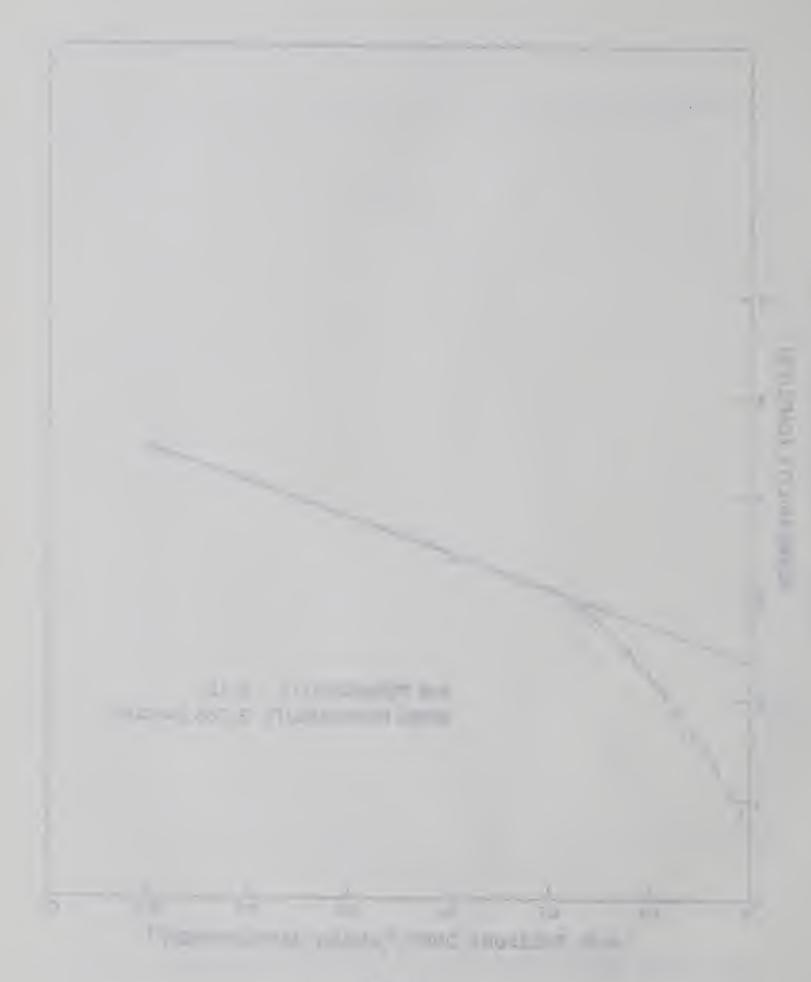


FIG. 3

KLINKENBERG PERMEABILITY OF THE ARTIFICIAL CORE PACK



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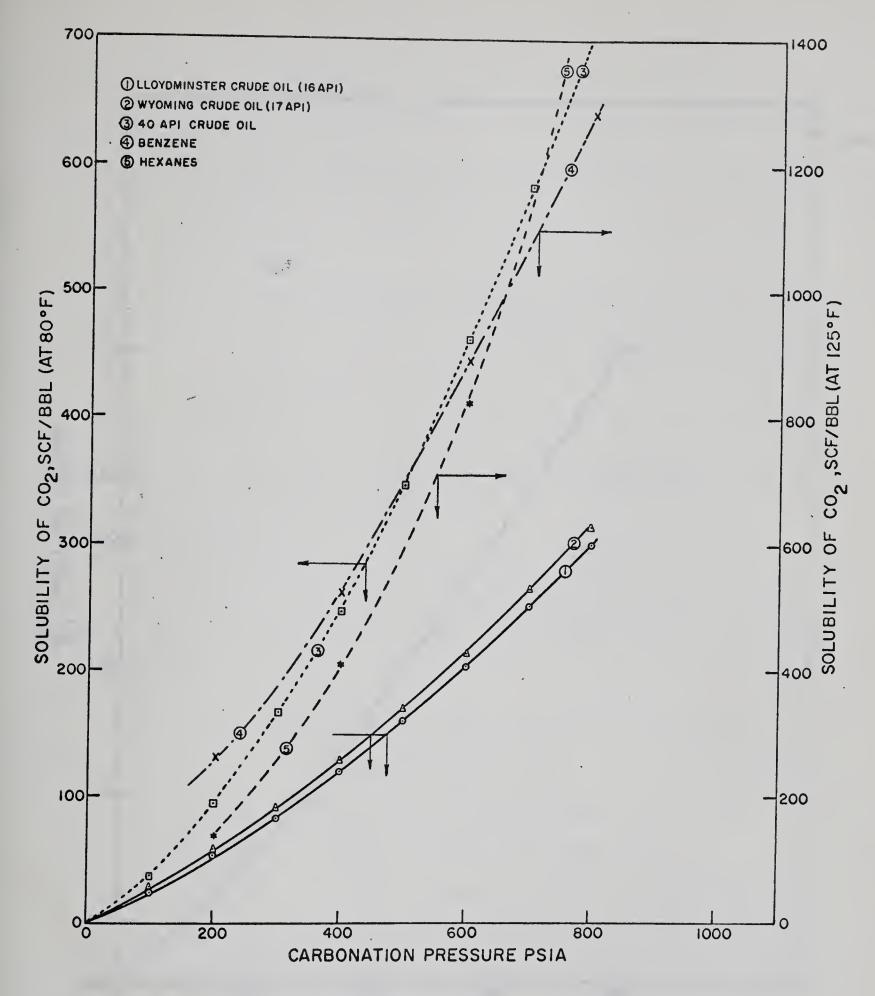
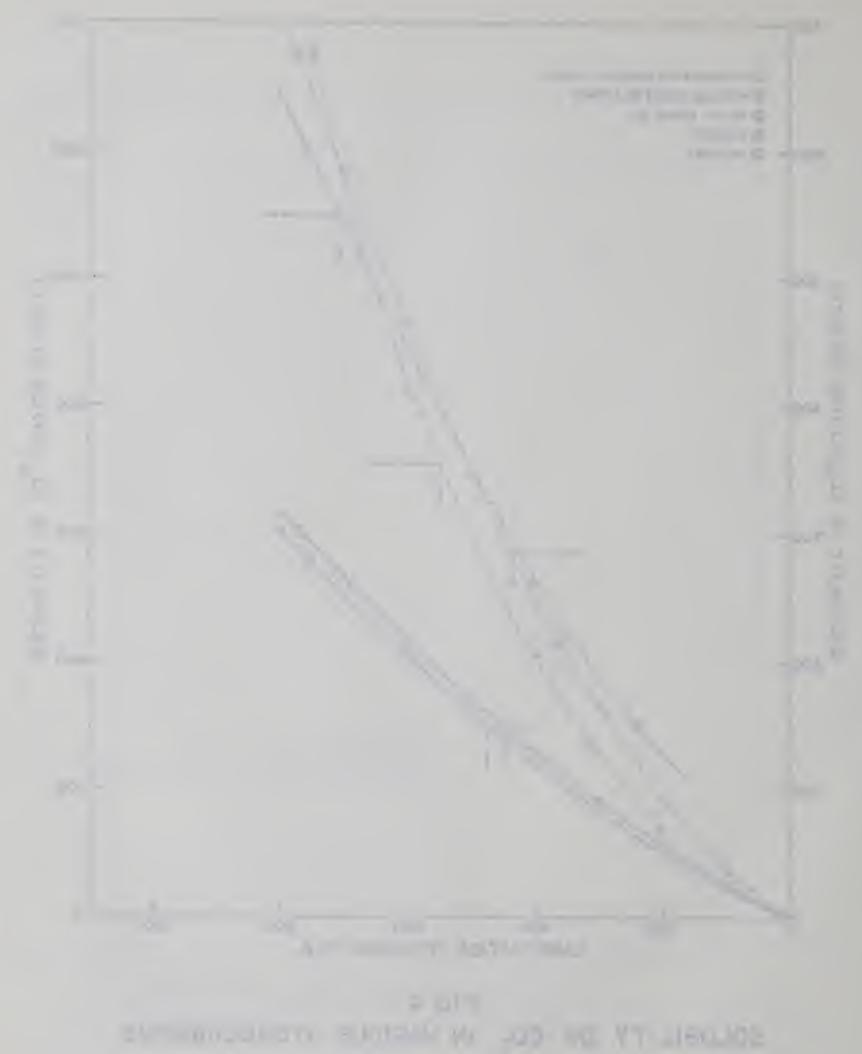


FIG. 4
SOLUBILITY OF CO₂ IN VARIOUS HYDROCARBONS



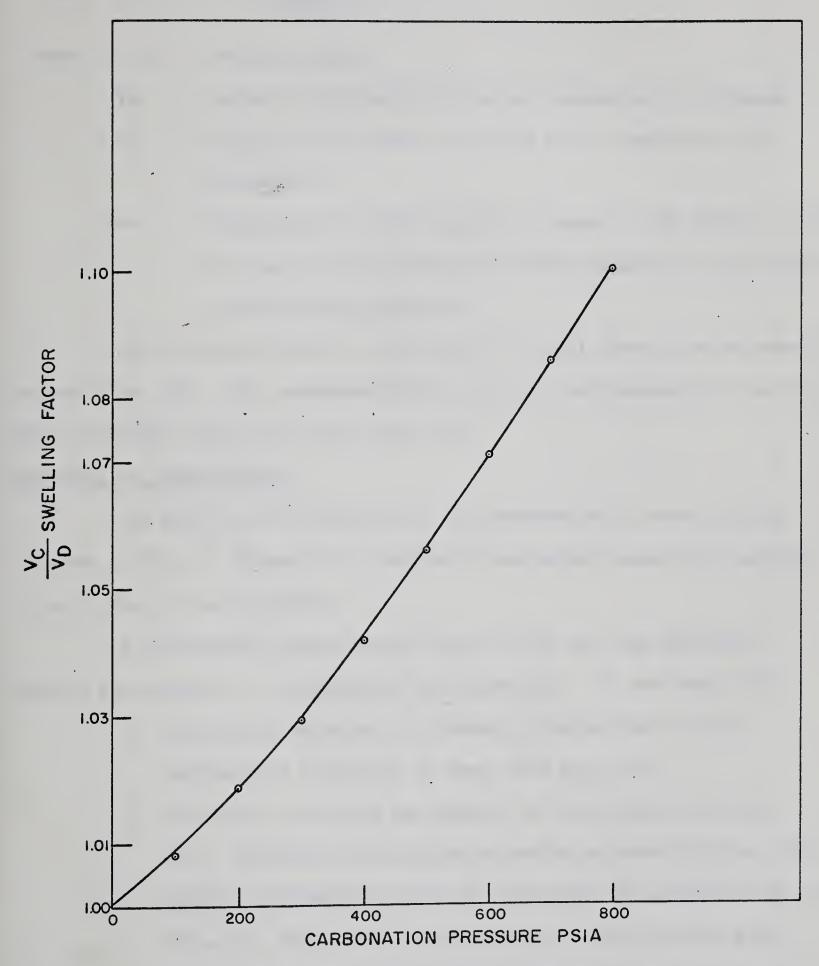
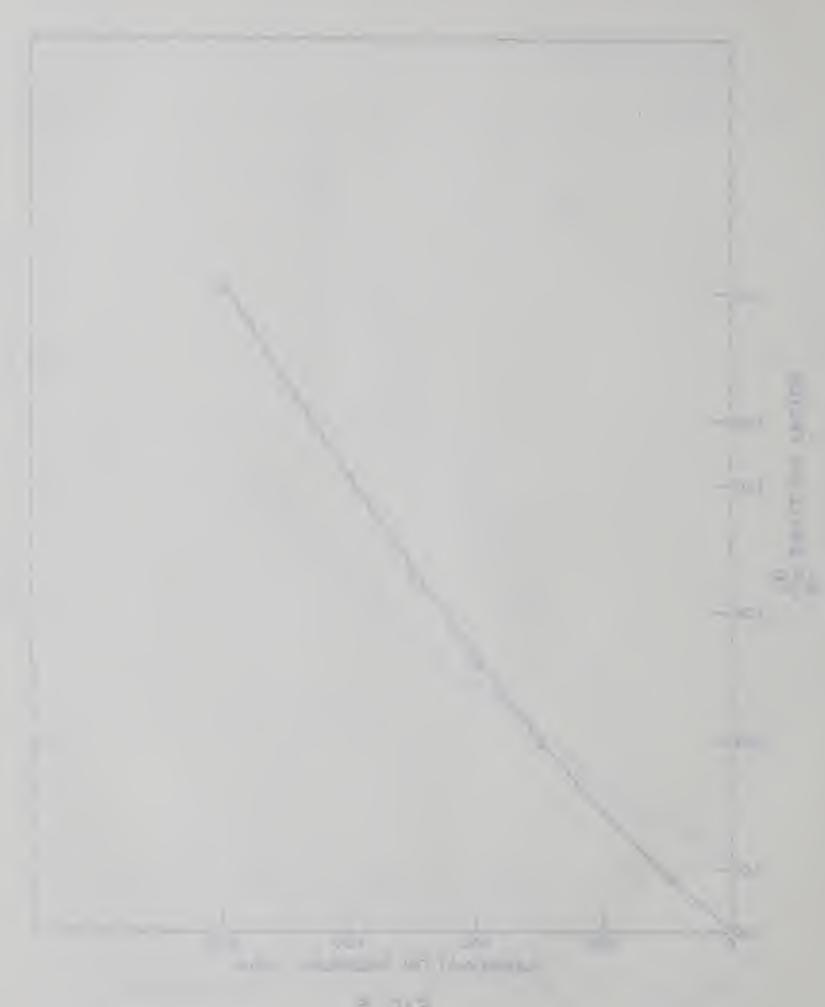


FIG. 5
SWELLING FACTOR FOR CARBONATED 16.0 API
LLOYDMINSTER CRUDE OIL



SWELLING PROTEIN TOR CARSONITAD INDIANA

S.F. =
$$\frac{\text{Vc}}{\text{Vd}}$$

and S.F. = 1 + $\frac{0.35 \text{ (Rsc.)}}{1000}$ (at 80°F)

where S.F. = swelling factor

Vc = volume of carbonated oil at the temperature and pressure.

Vd = volume of this dead oil in cell at the temperature and pressure.

Rsc. = Solubility of carbon dioxide in crude oil SCF (60°F & 1 atm.)

per barrel of dead state oil at the temperature under which

solubility was measured.

As the carbon dioxide is dissolved in the oil there is an increase in volume of the oil. This increased volume of the oil is produced from the core, which otherwise would have left in the core.

Viscosity of Carbonated Oil

The effect on the viscosity of oil saturated with carbon dioxide is shown in Fig. 6. Viscosity in centipoise was plotted against the pressure at which the oil was saturated.

A considerable amount of data (21,4,22,23) had been published showing the reduction in viscosity of carbonated oils. It was noted that:

- 1) The maximum reduction in viscosity occurred when oil was saturated at a pressure of about 1000 psia (17).
- The percent reduction was greater for the higher viscosity oils. Certainly the absolute reduction was more striking. For example, Lloydminster crude oil (1160 cps) was reduced to 30 cps. (Fig. 6). With Aneth crude reduction in viscosity was about 23% when saturated with carbon dioxide at 800 psia. A low reduction in viscosity was typical of low viscosity crude oils.

It was suggested (5) that carbon dioxide when in solution in the hydrocarbons reacted slowly to form certain organic compounds with hydrocarbons.

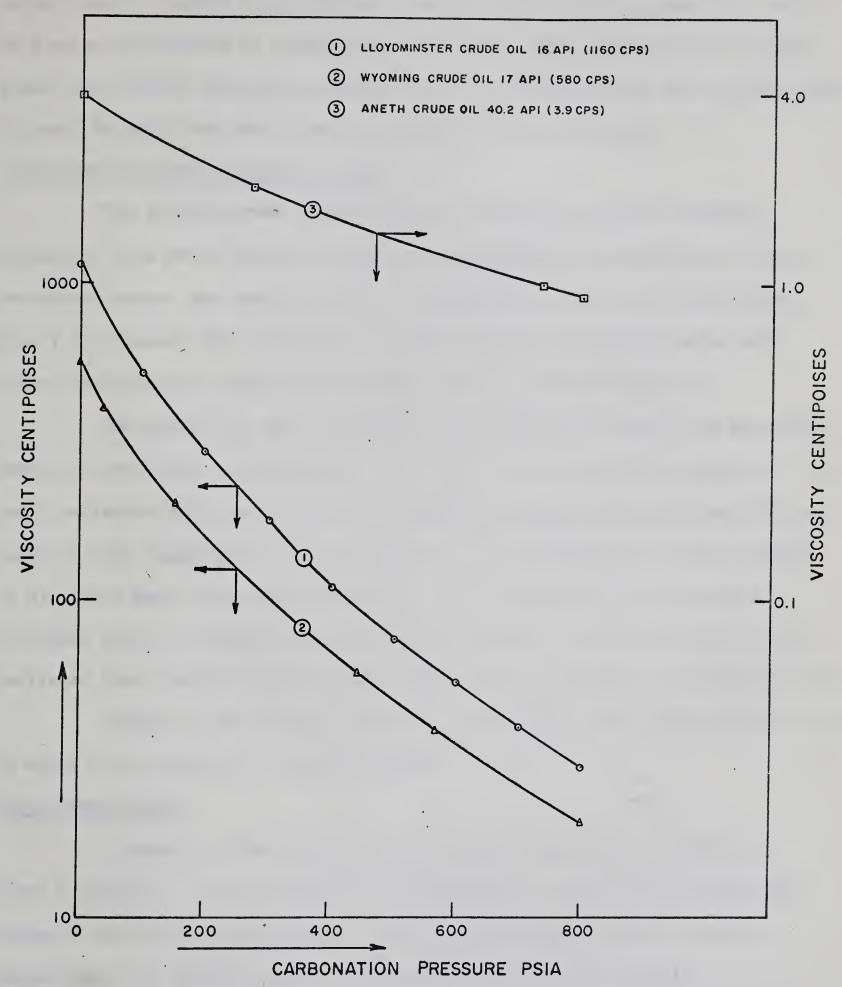
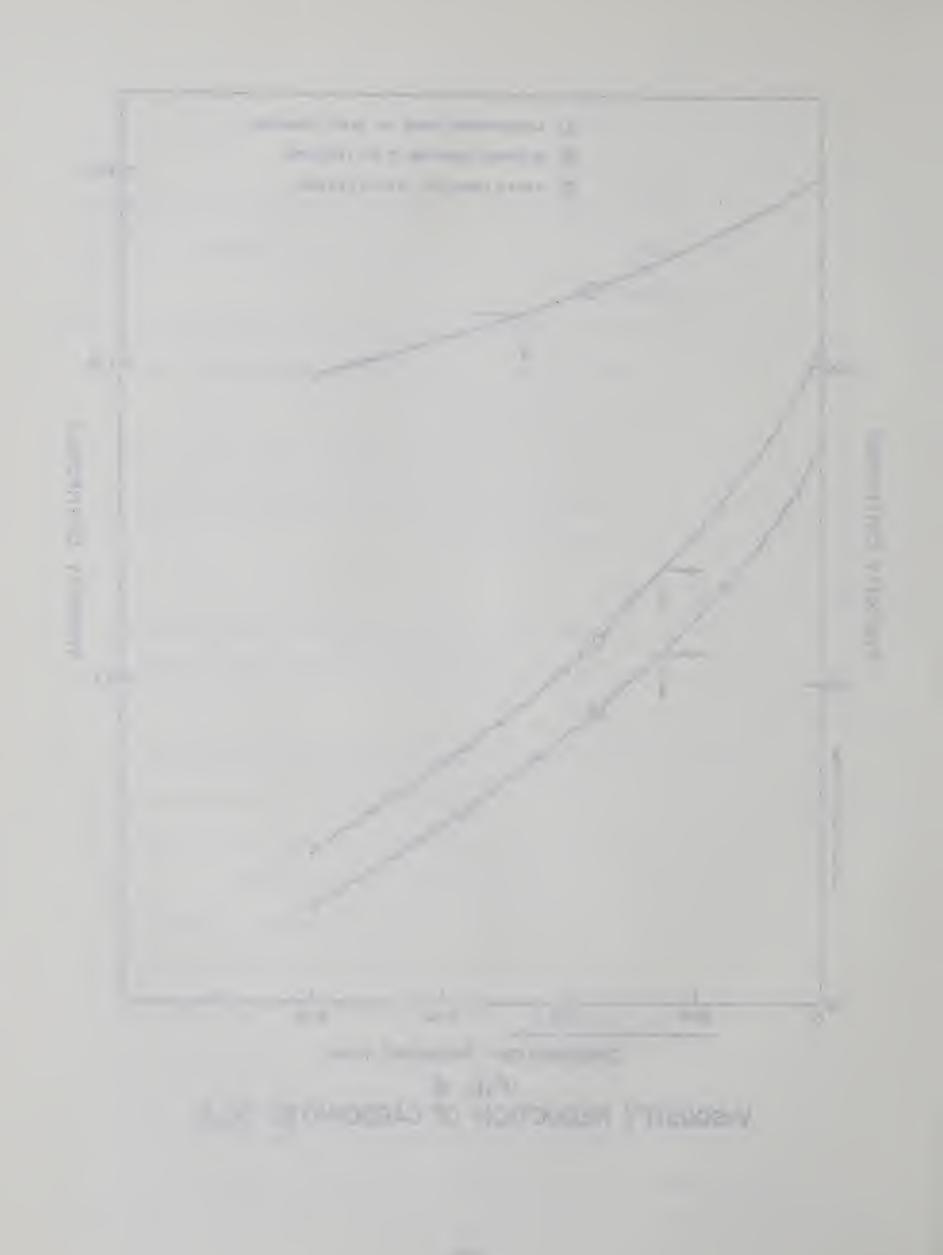


FIG. 6
VISCOSITY REDUCTION OF CARBONATED OILS



Carbon dioxide reacted on petroleum crudes as a mild oxidizing agent and tended to form such compounds as aldehydes and the lower fatty acids and their soaps.

These newly formed compounds were much lower in viscosity than the original crude. It could be said that they acted as solvents for the crude oil.

Solubility of Carbon Dioxide in Water

The solubility of carbon dioxide in water was another important property. This would determine how much carbon dioxide was available in the reservoir through the carrier to give the beneficial effects to displacement. Fig. 7 illustrates the solubility of carbon dioxide in distilled water and brine. Solubility increased with an increase in saturation pressure.

The solubility of natural brine was compared with that from Holm (17) having the same salt concentration. The two curves were in fair agreement. The small variation might be due to some temperature change as the measurements were taken at room temperature. Curve number 3 is the solubility of carbon dioxide in distilled water taken from literature. This indicates that solubility decreases with an increase in the salinity of water. It was also observed from published data that the solubility decreased with an increase in temperature (17).

Jhonson et al (3) showed that there was very little effect on the viscosity of water by the addition of carbon dioxide.

Displacement Tests

A summary of the initial test conditions and final recoveries is shown in Table I. In the present study temperature, rate of displacement and viscosity ratio were kept constant. Only the carbonation pressure or the concentration of carbon dioxide in the displacing fluid was changed.

On reviewing the initial conditions it may be noted that there was a gradual increase in the irreducible water saturation as the concentration of carbon dioxide in the displacing fluid increased. This is believed to indicate an increase in water wettability of the system. It has been shown on tests with

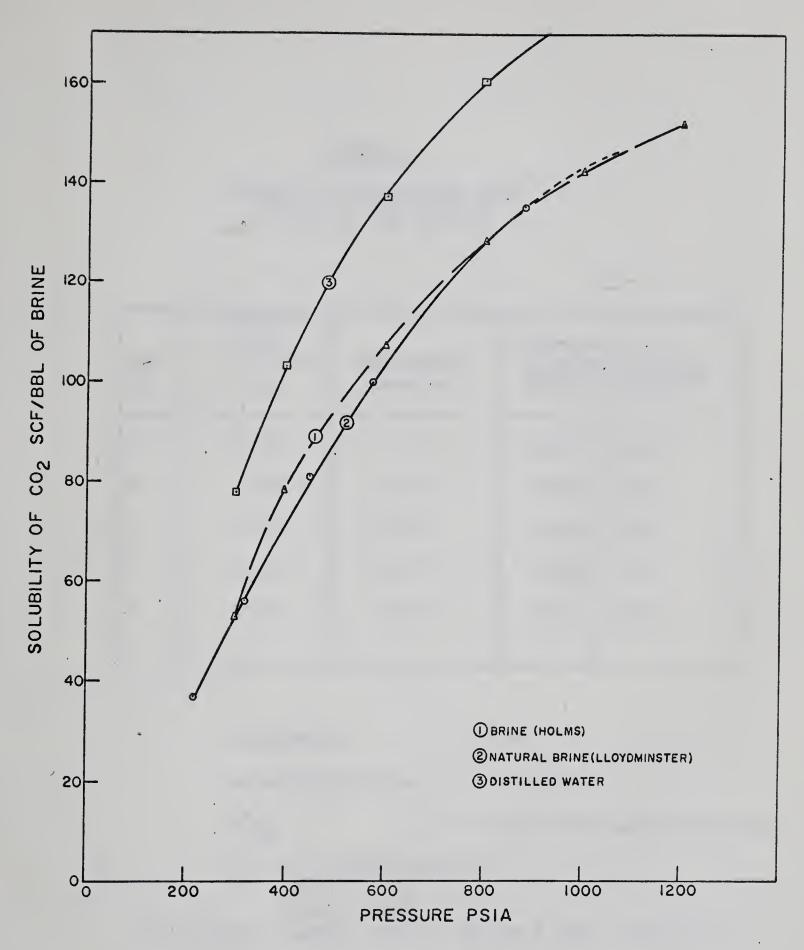


FIG. 7
SOLUBILITY OF CO₂ IN BRINE (6.78%) AT(78°F)

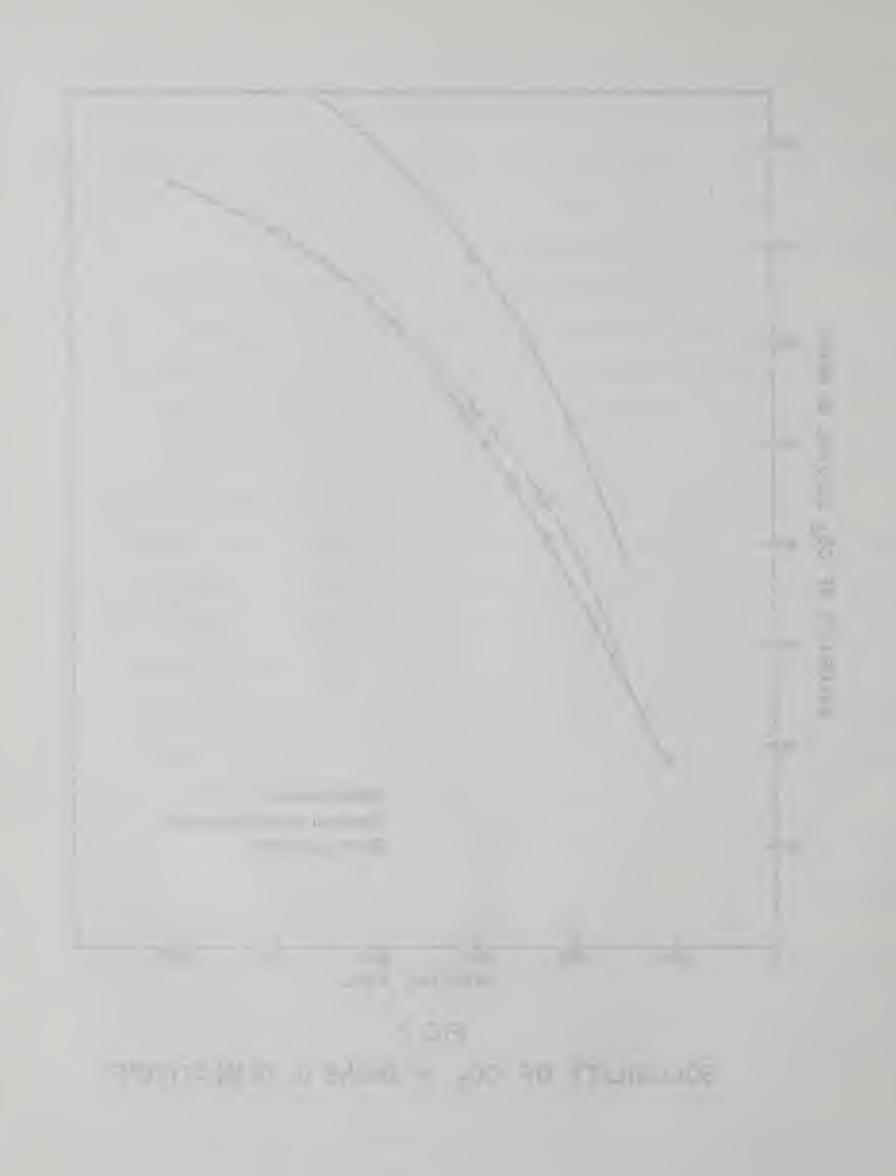


TABLE I
SUMMARY OF DISPLACEMENT TEST
CONDITIONS AND RESULIS

Run No.	Initial Water Saturation ^S wi	Carbonation Pressure		tive Oil by Fraction Wi=2P.V.
1	0.092	-	0.207	0.326
2	0.146	350	0.213	0.383
3	0.217	580	0.317	0.540
4	0.357	720	0.613	0.686
5	0.414	890	0.82	0.833

temperature = $80^{\circ}F$ rate of injection = 10 cc/hr. U_0^*/U_W = 1126.2 (for brine flood only) U_0^* is pressure sensitive

- The recovery figures shown in Column 4 were obtained for a water-oil ratio cut-off of 5 and those in Column 6 for a cumulative injection of two pore volumes -



carbonates, bicarbonates, borates, silicates and acetates of Group 1 elements that these chemicals destroy the affinity of oil for sand. Uren and Fahmy (24) further developed this hypothesis by considering the following reactions:

The carbonate in the present case would be formed by the interaction of the carbonic acid with some other salts. Beckstrom and Van Tuyl (25) noted a definite reaction between sodium carbonate and sandstone similiar to that suggested by Nutting and Uren.

As more and more of the carbonated water contacts the sand grains, it removes the adsorbed or bonded semi-organic films on the mineral surfaces of the sand pores and thus renders the surface preferentially water wet. In the present case the increase in the irreducible water saturation is believed to be caused by the change in the wettability of the core rendering it more water wet.

Brine Displacement Test

One regular brine flood was run on the core pack to establish the basic characteristic of the flood performance. This flood data also provided a basis for comparing the carbonated brine flood recoveries.

The initial water saturation for the first test was 0.092. This connate water saturation was less than that obtained by Collins (18) and Scott (19) in their work. This might be due to the particle size distribution of the core used in this study. The lower initial water saturation as compared to Collins' work might be due to a difference in the wettability characteristic of the core. Collins' core was more water wet whereas in the present study the core was believed to be slightly oil wet or neutral.

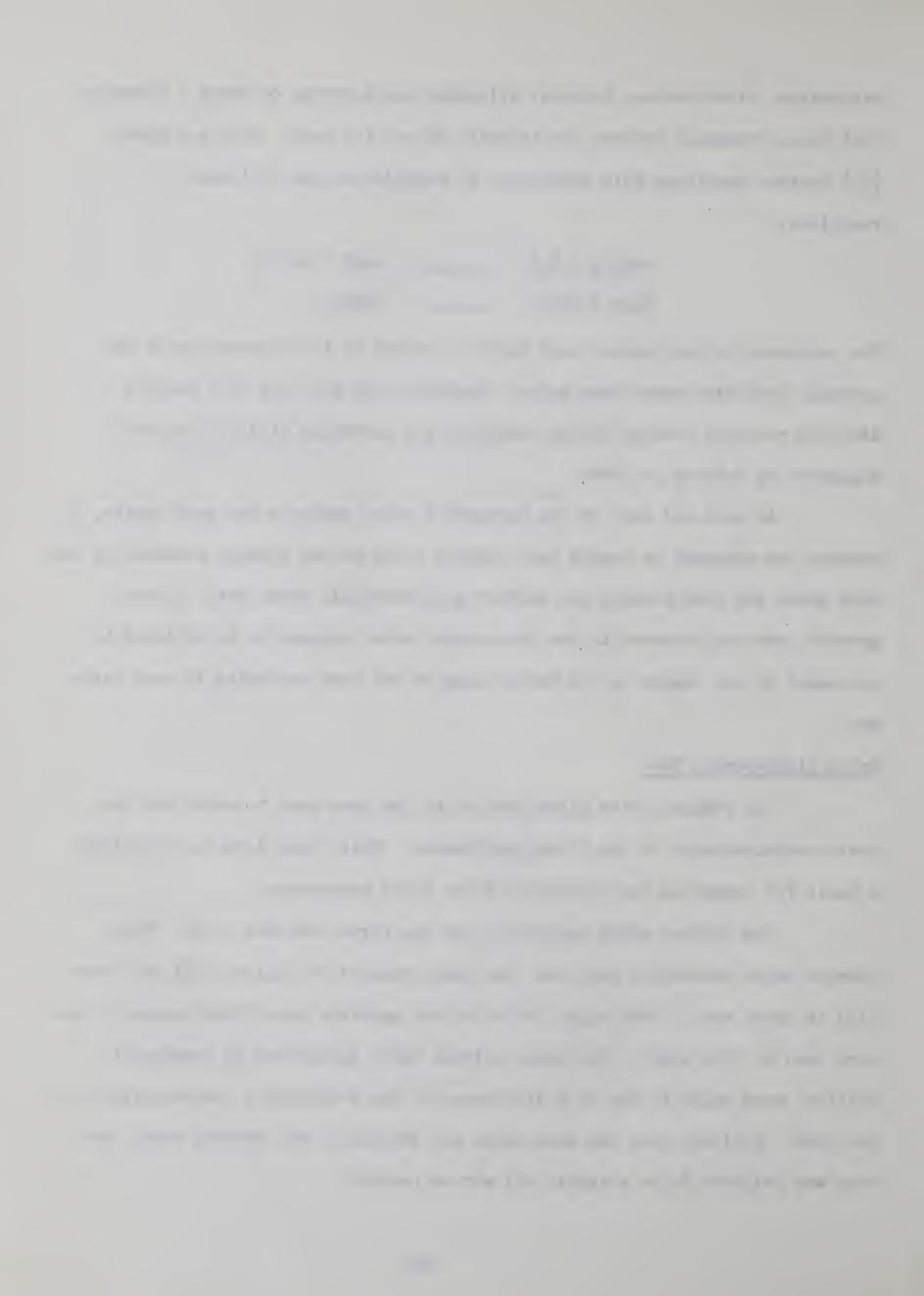


Fig. 8 shows a comparison of brine flood recovery with the work of Scott and Collins. The sand and crude oil used in this study and that of Scott were the same, whereas Collins used a different sand system. The brine flood recovery of the present work and that of Scott compare favourably where as Collins found a higher recovery. The difference might be due to difference in wettability of the cores.

The Welge (26) method was used to determine the unsteady state relative permeability results illustrated in Fig. 9 and Table B-7. From Fatt's work it was found that the position of the relative permeability curve was indictative of the wettability of the system. The initial conditions of the core seemed to be slightly oil wet or neutral when compared to Fatt's work. Collins' and Scott's cores appeared to be more water wet.

Fig. 10 was constructed based upon concepts of Loomis and Crowell (27) to find if the data used for the relative permeability was in the subordinate production zone. The break is caused by the presence of a stabilized zone which occupies a finite portion of the core sample for a short time and therefore affects a measureable portion of the production curve. The break defines the highest oil saturation for which the relationship between $k_{\rm W/k_{\odot}}$ and saturation would be valid. A change in the slope of the fractional oil flowing curve was evident at about 0.5 pore volume of cumulative injection. The earlier portion where there was more oil flowing was called the frontal zone, which was interpreted to be dispersed zone of high water saturation: the later part was referred to as the subordinate production zone.

In floods 3,4, & 5 however, it was observed that there was an increase in the fraction of oil flowing after about one pore volume was injected. This was likely the effect of carbon dioxide diffusing into the oil. This brought about a decrease in the viscosity of oil, a decrease in interfacial tension of water and oil, an increase in its mobility and a volume expansion of the oil in

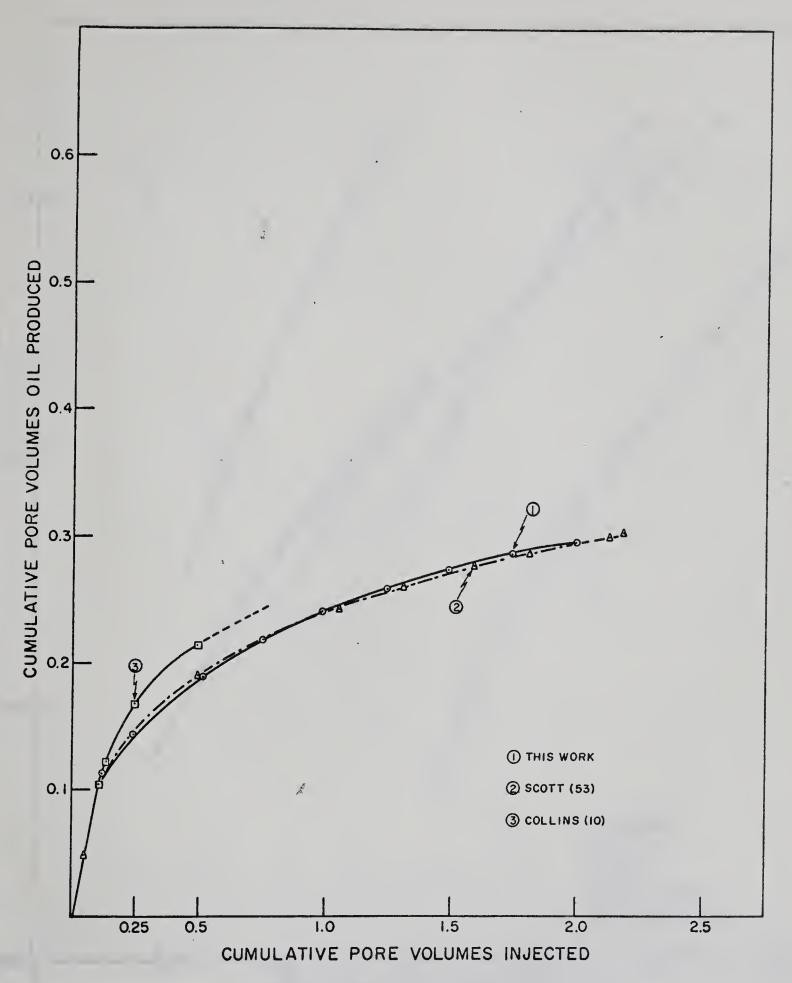
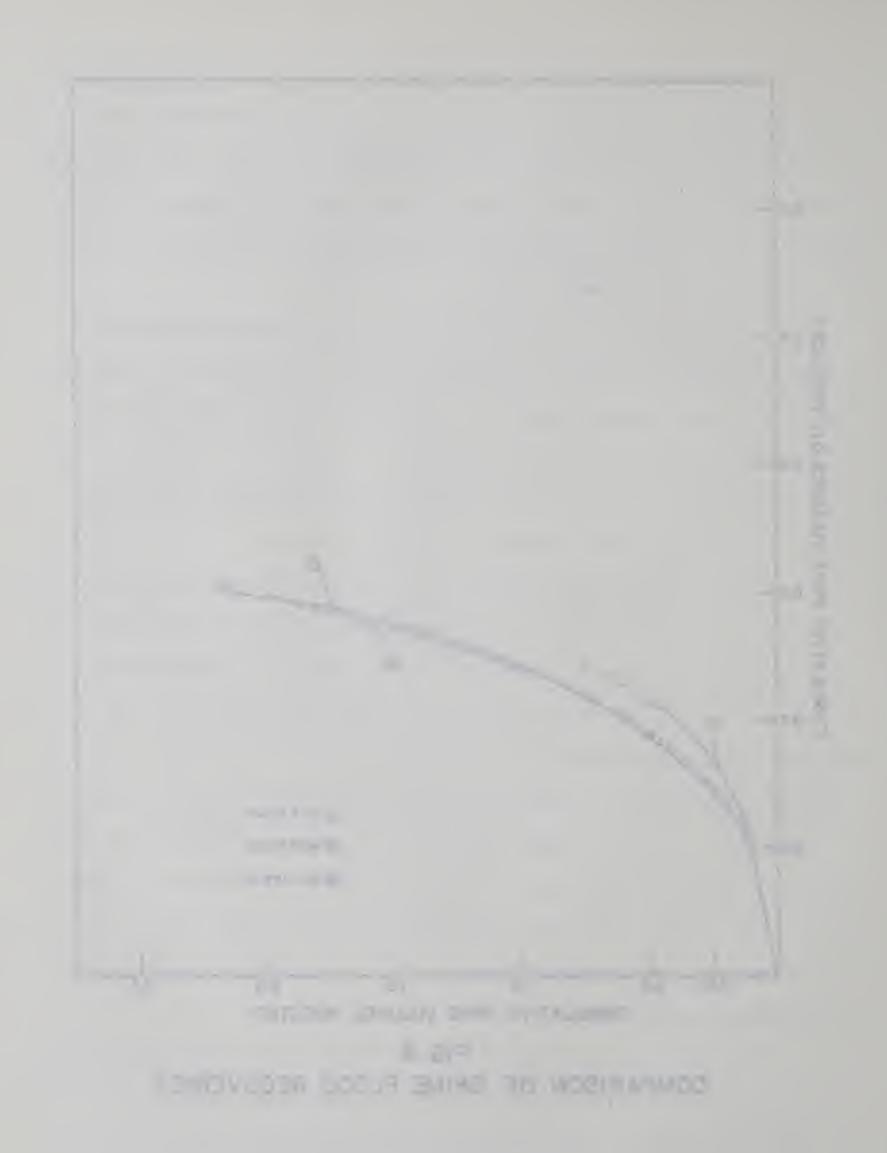


FIG. 8

COMPARISON OF BRINE FLOOD RECOVERIES



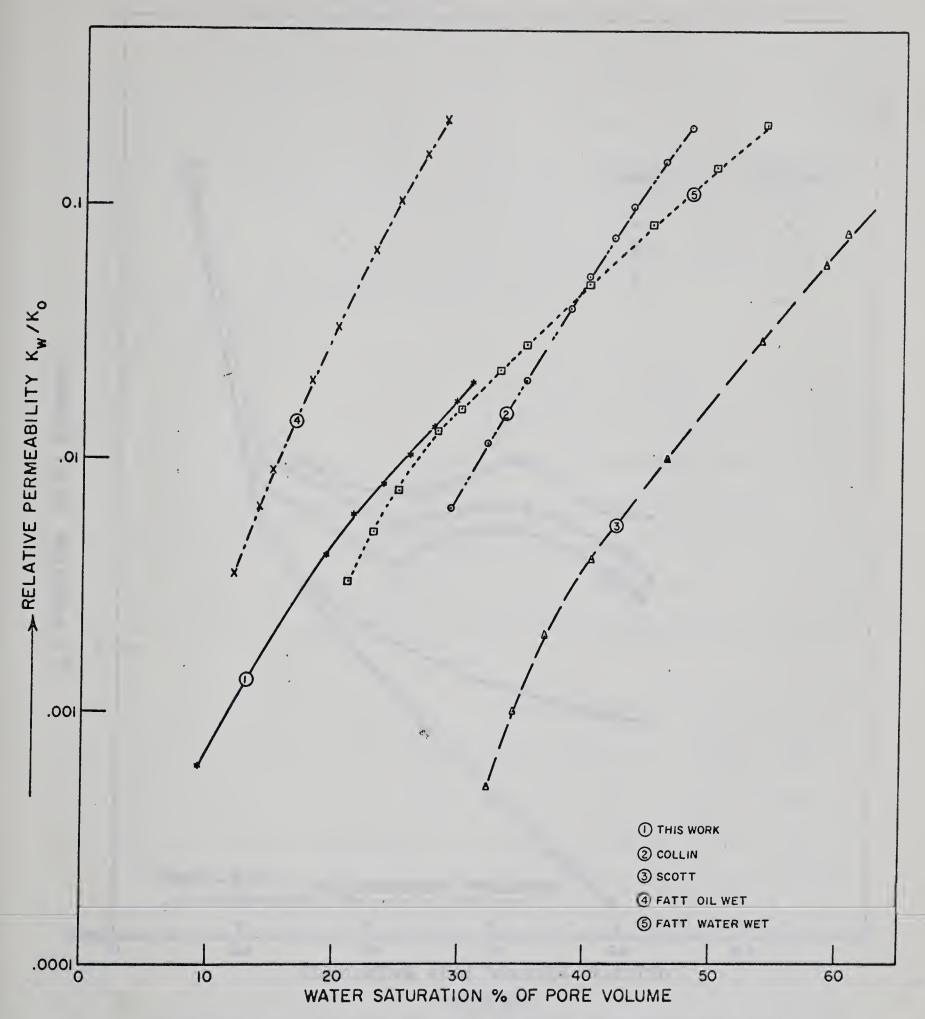
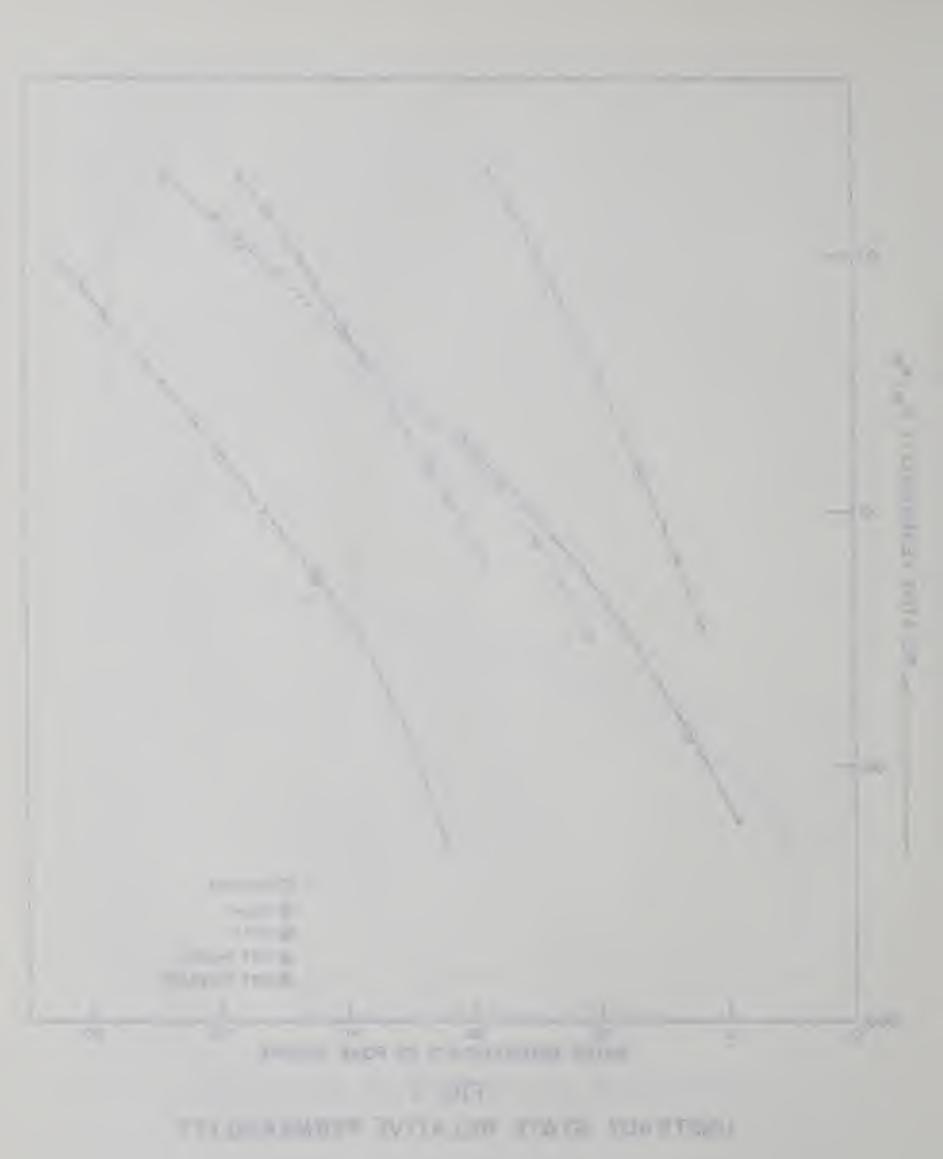


FIG. 9
UNSTEADY STATE RELATIVE PERMEABILITY



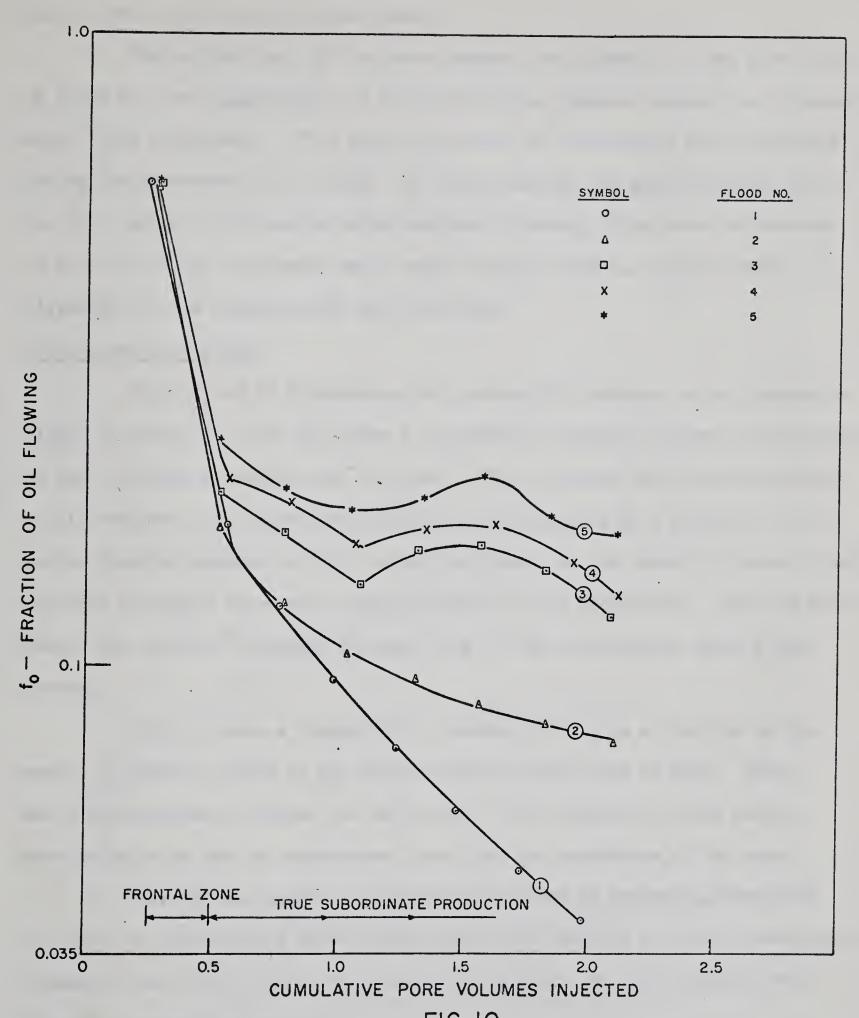


FIG. 10
FRACTIONAL FLOW OF OIL AFTER BREAKTHROUGH
INDICATING PRESENCE OF TWO FLOW REGIMES

place, after the flood front had passed.

The earlier part of the curve between the injection of one pore volume of fluid and the disappearance of the frontal zone appeared similar to a conventional water flood performance. This was in line with an interesting factor observed during the carbonated brine flood. No carbon dioxide was produced until about one pore volume of carbonated water had been injected. This was also observed by Holm (20). The carbonated water being miscible with the connate water, it displaced all the connate water and oil first.

Carbonated Brine Floods

Fig. 11 and 12 illustrates oil produced in relation to the cumulative fluids injected. In both the cases a substantial increased recovery was realized as the carbonation pressure was increased. Fig. 13 shows the percent increase in oil recovery over conventional brine flood recoveries as a function of the carbon dioxide injected per unit of oil in place. As the amount of carbon dioxide injected increased there was a large increase in oil production. Over the range tested the recovery increased to about 150% of the conventional brine flood recovery.

Fig. 14 shows a comparison of recovery of oil as a function of the amount of carbon dioxide in the displacing fluid with that of Holm. There was a fair agreement between the two curves. The difference in the middle portion might be due to experimental error and the properties of the core.

There were a number of factors which aided in recovering the extra oil over the conventional water floods. All these factors were not investigated separately under the present study but all contribute to some extent to the increased recoveries observed.

Carbon dioxide reacts with some of the components of crude oil to form polar compounds. It has been found that these compounds have a marked effect in lowering the interfacial tension between the oil and the water.

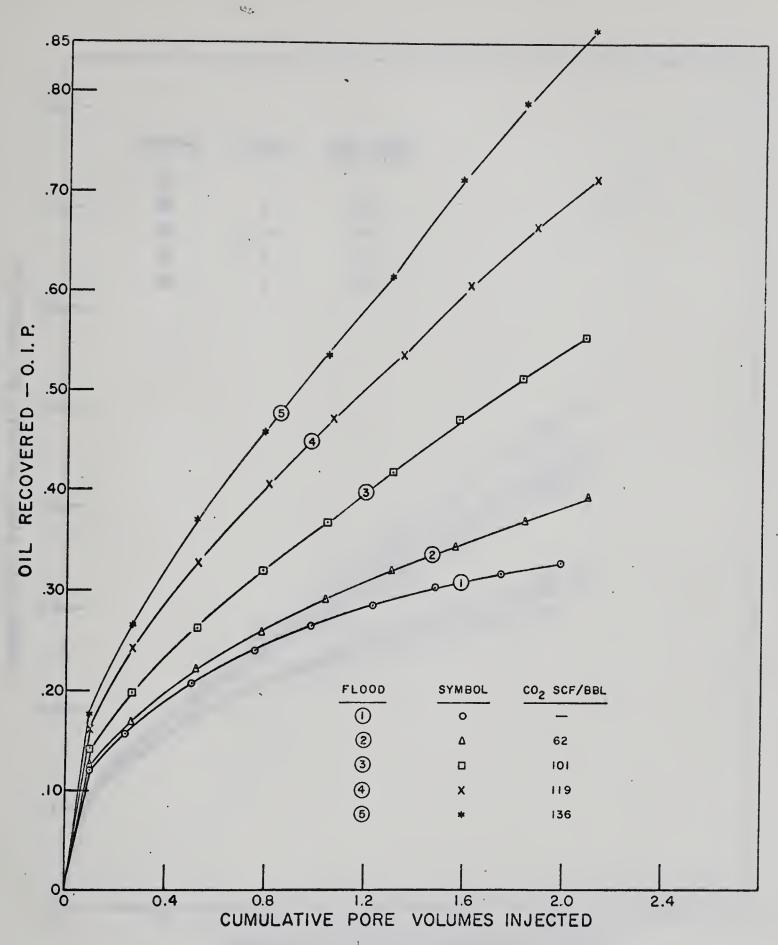
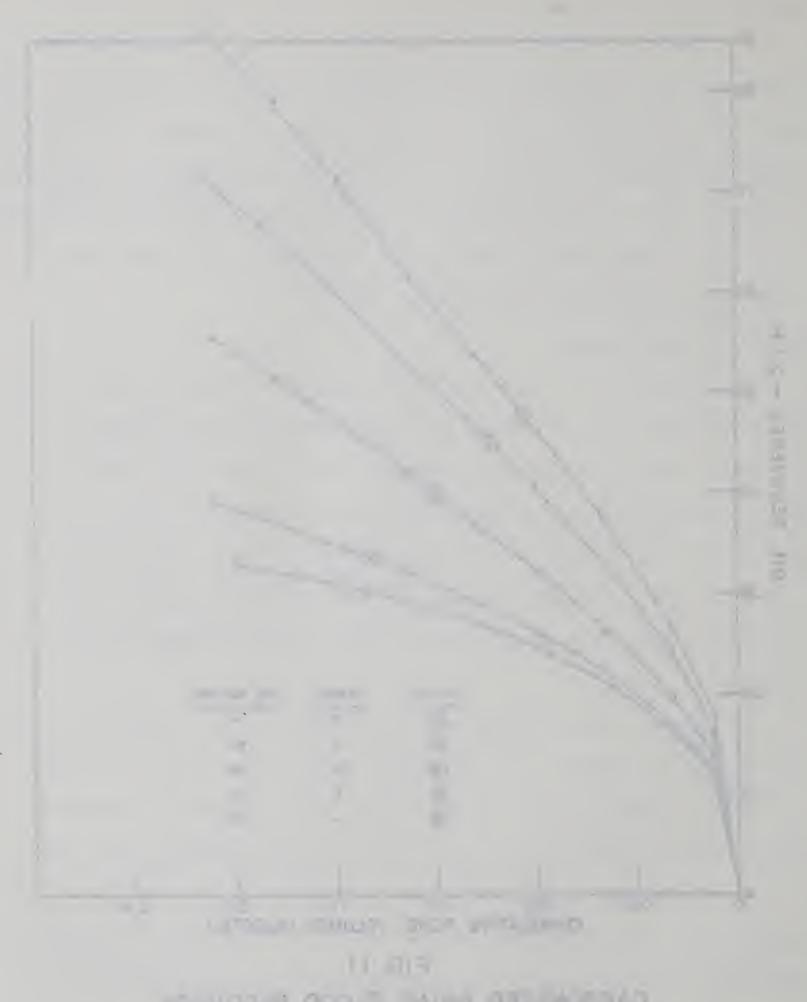
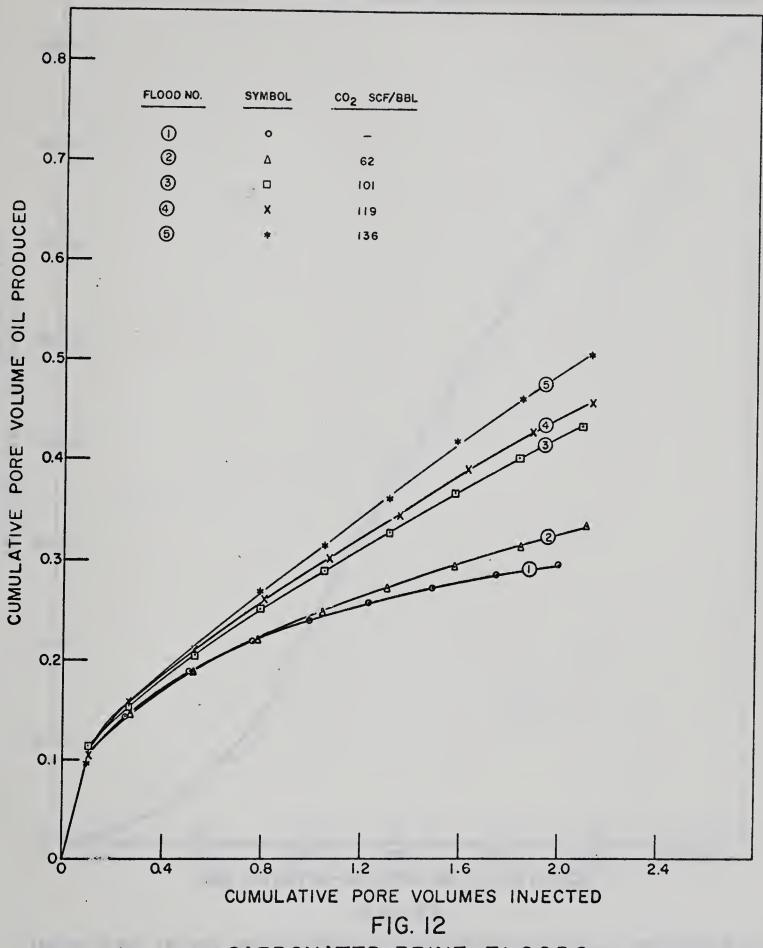


FIG. II

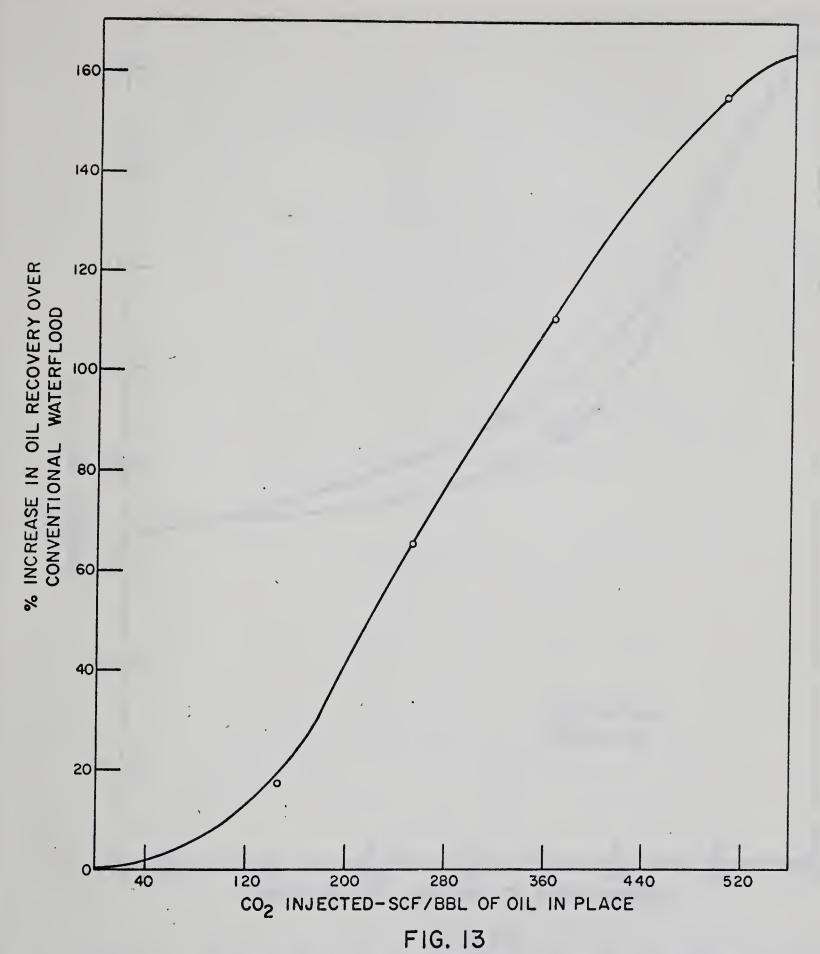
CARBONATED BRINE FLOOD RECOVERY



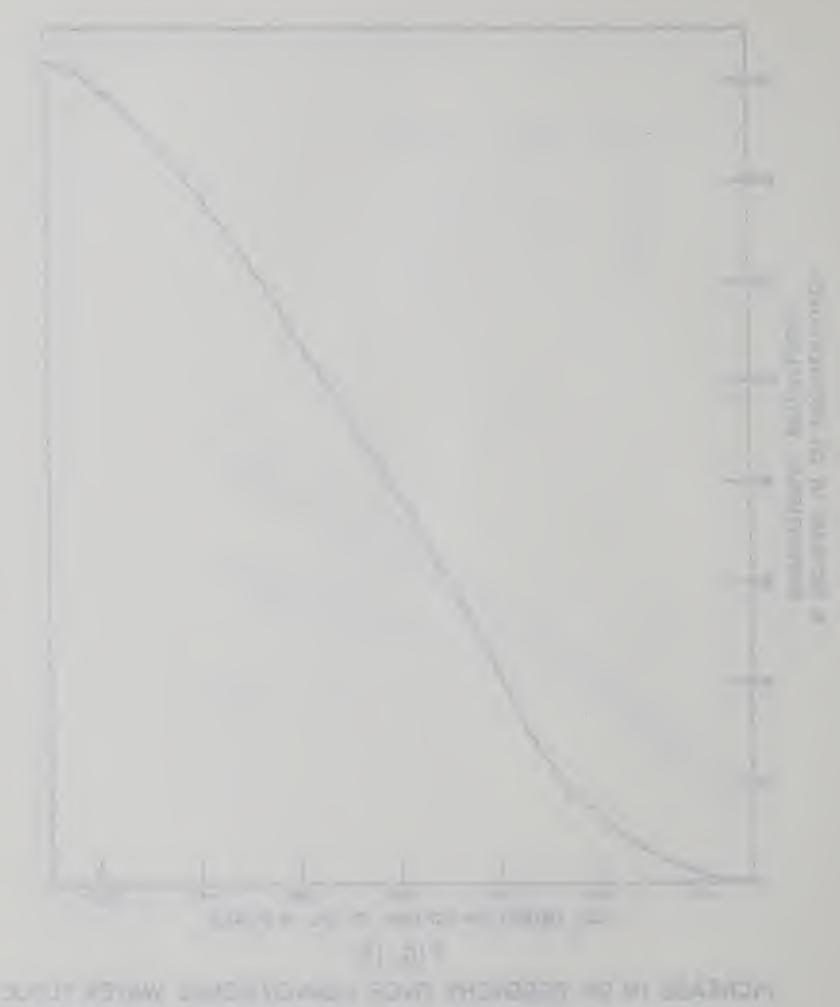


CARBONATED BRINE FLOODS

ECOSES WERE WILLIAM DE



INCREASE IN OIL RECOVERY OVER CONVENTIONAL WATER FLOOD



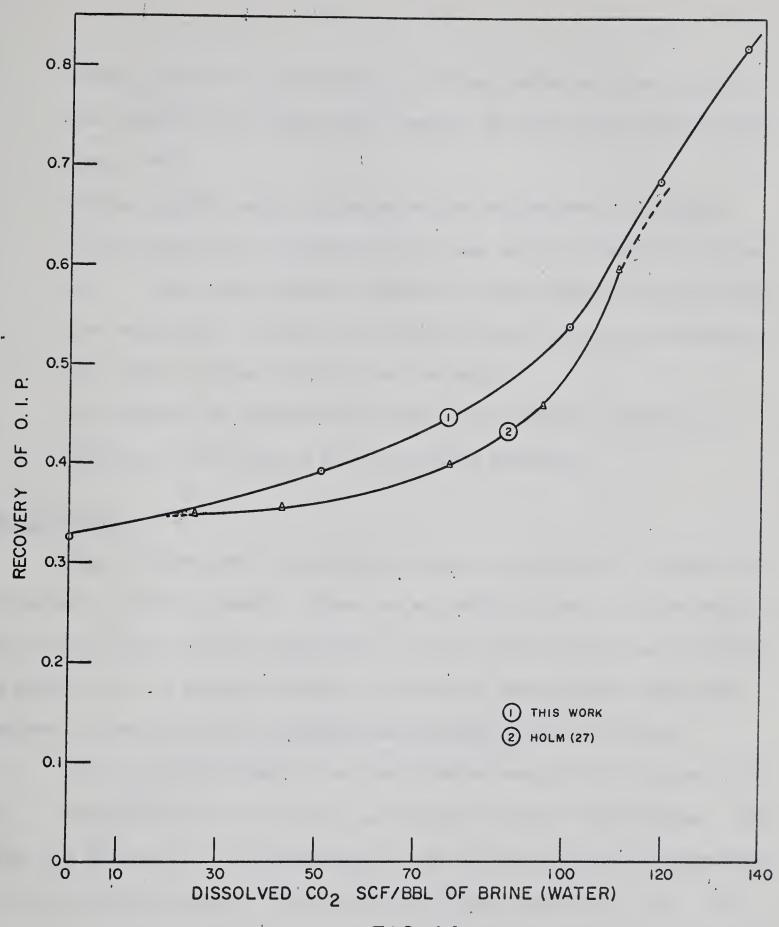
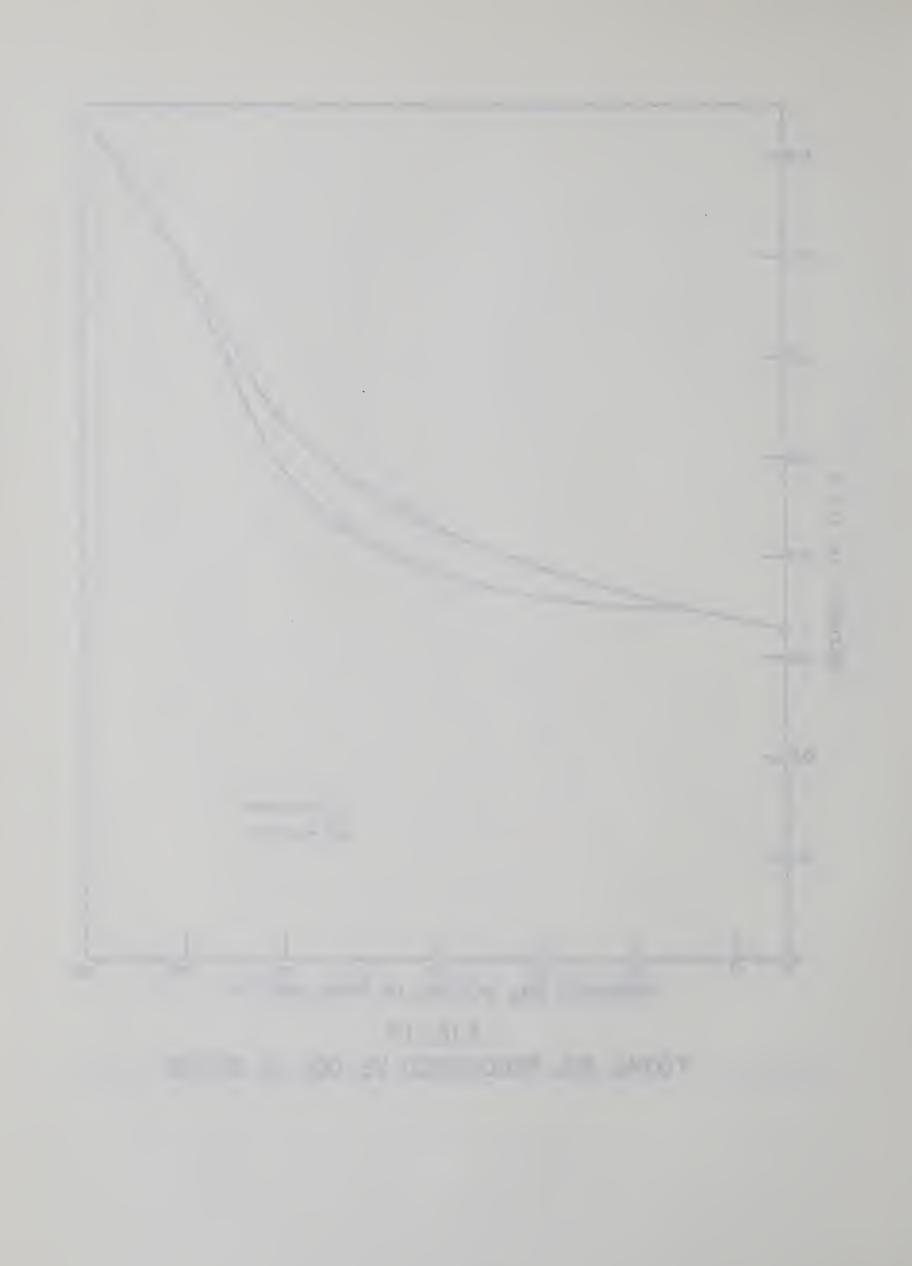


FIG. 14
TOTAL OIL RECOVERED VS. CO₂ IN BRINE



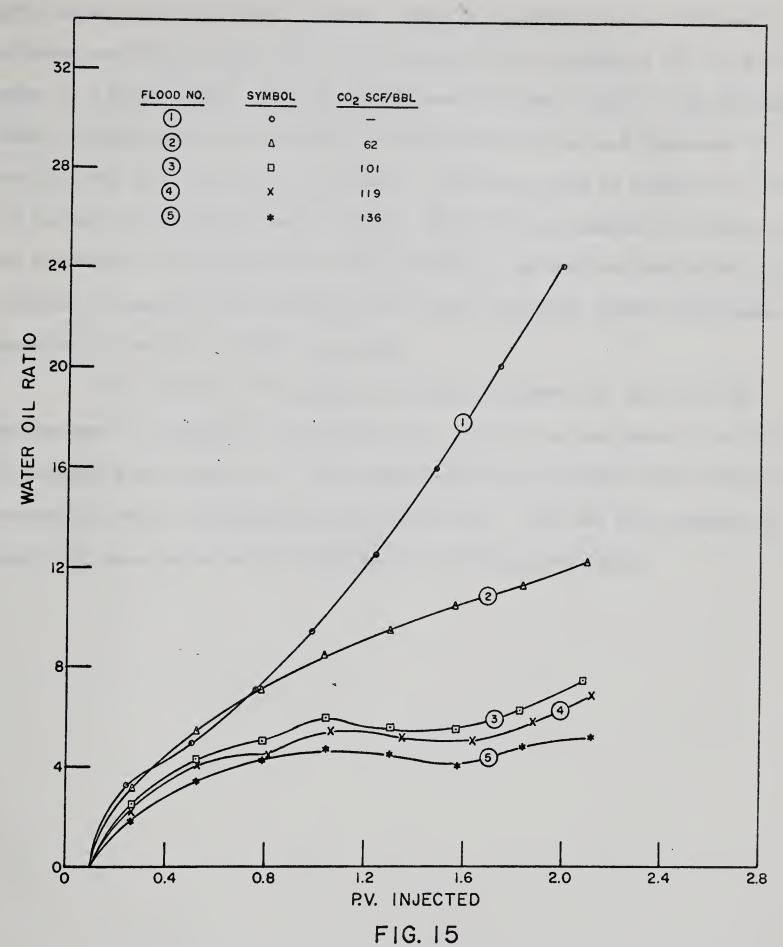
- 2) Carbon dioxide is soluble both in oil and water and thus contacts the surface of the sand grains whether the sand grain was water wet or oil wet.
- Carbon dioxide under high pressure has the property of forming loose compounds or (complexes) with some of the components of crude oil. These newly formed compounds are much lower in viscosity than the crude oil. It has been suggested that they act as solvents for the crude oil thus reducing the viscosity.
- The presence of carbon dioxide tends to minimize the swelling of clays and thus render a dirty sand more permeable.

Water Oil Ratio

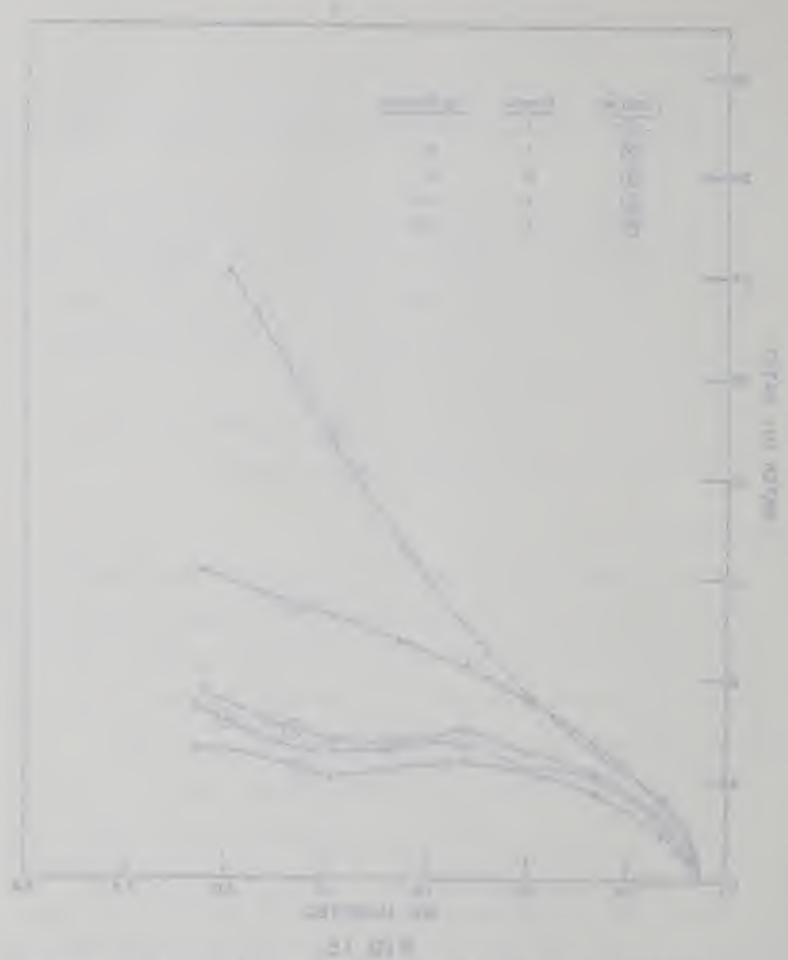
Fig. 15 shows the relationship of water oil ratio as a function of the cumulative fluid injected. There was an overall decrease in the water oil ratio as the carbon dioxide concentration of the injected water was increased. This agrees with the general results of carbonated water floods which show increased oil production and consequently decreased water oil ratios.

Curve 1 is for a brine flood and shows a sharp rise in the water oil ratio. Curve 2 crosses over Curve 1 in the earlier part of the flood. This is due to a decrease in the temperature of the oil bath during the second run. There is a distinct anomaly in the curves for floods number 3, 4 & 5. The maximum point in the earlier part of the water oil ratio curve might be related to the following phenomena.

It was observed in these runs that no carbon dioxide was produced



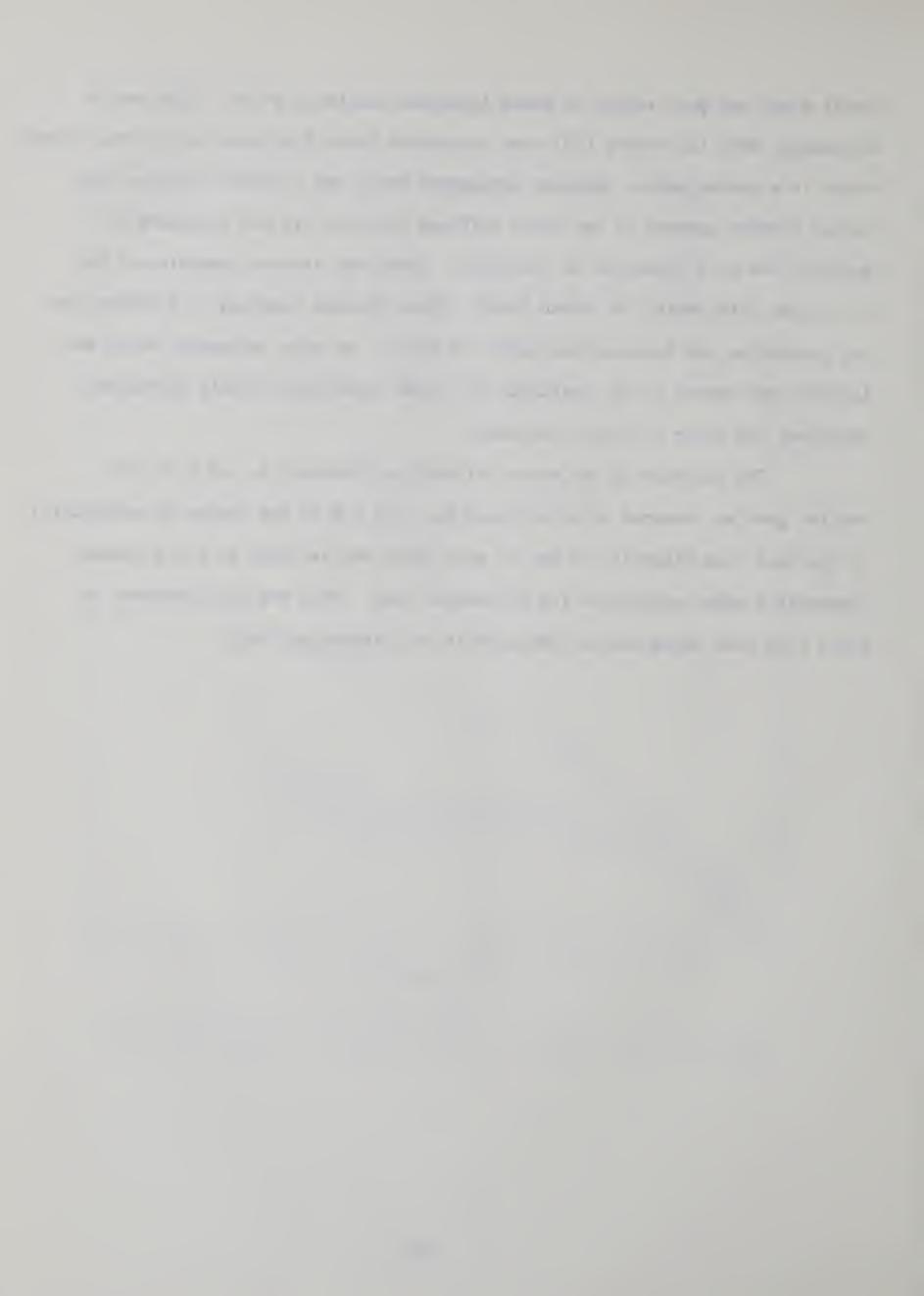
WATER OIL RATIO IN RELATION TO FLUID INJECTED



DETERMINED TO SECURE AT CASE OF STREET

until about one pore volume of total injection had taken place. This was in accordance with the theory (20) that carbonated brine displaced the oil and connate water in a porous media. As more carbonated brine was injected into the core, carbon dioxide present in the brine diffused into the oil and increased its mobility due to a reduction in viscosity. There was also an expansion of the oil volume left behind the water flood. These factors combined to increase the oil production and decrease the water oil ratio. As more carbonated water was injected the amount of oil available for these beneficial effects decreased, therefore the water oil ratio increased.

The decrease in the water oil ratio of floods 3,4, and 5 in the earlier part as compared to brine flood No. 1 is due to the change in wettability of the core from slightly oil wet to more water wet as found by the increased irreducible water saturation for successive runs. This was also observed by Scott (19) when using sodium hydroxide in the displacing fluid.



CONCLUSIONS

The following conclusions may be drawn on the basis of the present investigation regarding the effect of carbonated brine flooding on the recovery of heavy crude oil.

- 1) Total oil recoveries obtained by carbonated brine flooding were substantially higher than those obtained by conventional brine flooding.

 At a 5:1 water oil ratio cut off about 300 percent more oil was recovered with carbonated water (at 890 psia) as compared to brine.
- 2) The amount of oil production increased as the saturation pressure of carbonated brine was raised.
- 3) Carbonated brine flooding seemed to change the slightly oil wet or neutral sand towards a preferentially water wet system.
- The solubility of Carbon dioxide decreased with an increase in the salinity of the water.
- The solubility of Carbon dioxide in brine increased with pressure but decreased with temperature.

RECOMMENDATIONS

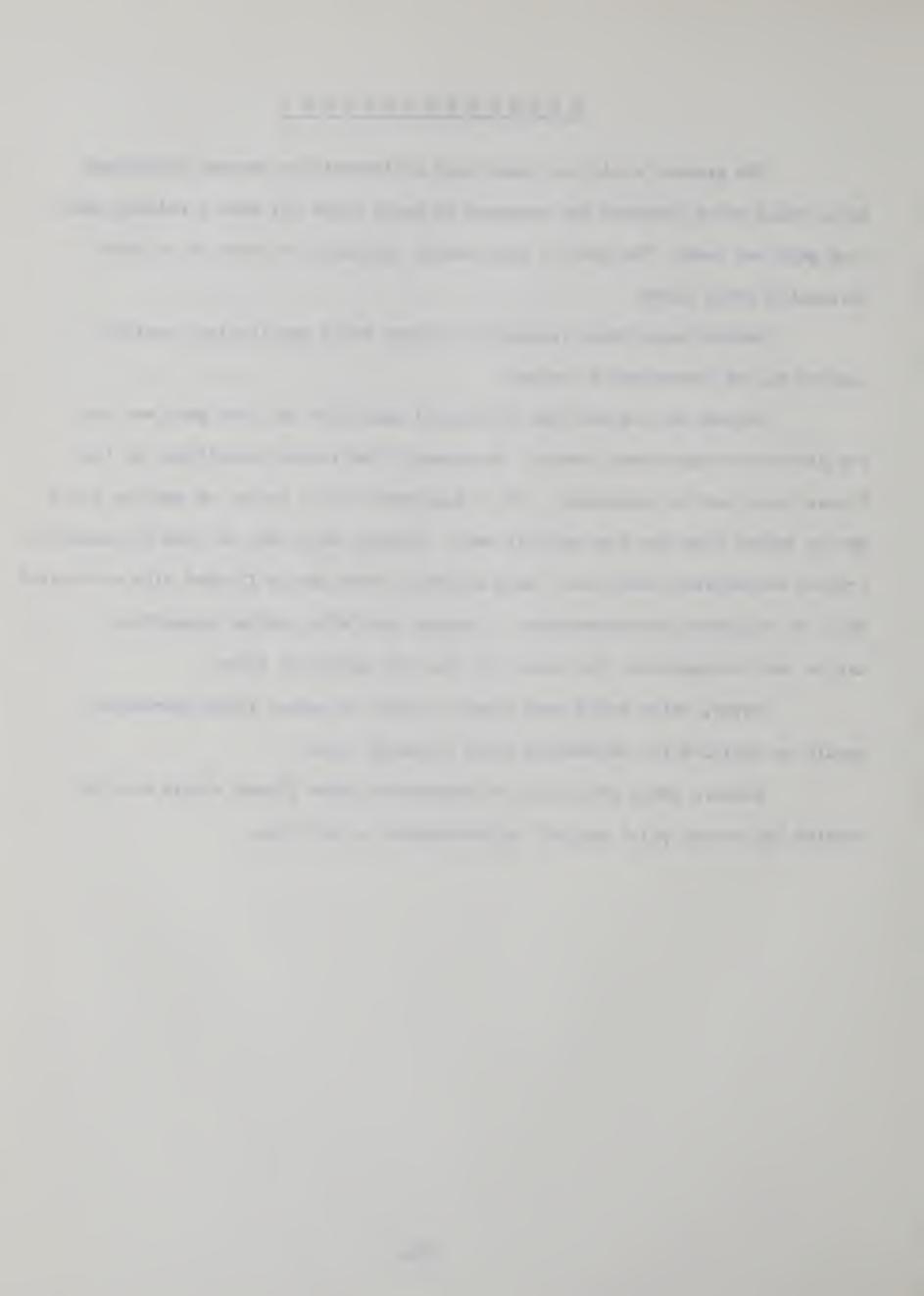
The present study was aimed only at determining whether carbonated brine flood would increase the recovery of heavy crude oil when a natural sand core pack was used. The present work showed increased recovery of oil with carbonated brine flood.

Before using these results for direct field application, certain aspects may be investigated further.

Because of the shortage of natural sand only one core pack was used for different displacement tests. As a result the initial conditions of the floods could not be reproduced. It is suggested that a number of smaller cores may be packed from the same natural sand. Natural brine may be used to establish initial saturation conditions. Each of these cores may be flooded with carbonated water of different concentrations. A longer core with similar properties may be used to duplicate the result of the most prominant flood.

Water, which would most likely be used in actual field operations should be utilized for carbonated water flooding tests.

Pattern sweep efficiency of carbonated water floods should also be studied before any pilot project is undertaken in the field.



LIST OF SYMBOLS

API - American Petroleum Institute

BS&W - bottom sediment and water

BT - break through

CO₂ - carbon dioxide

cc - cubic centimeter

cp - centipoise

^oF - Fahrenheit degrees

fw - fraction of water flowing

fo - fraction of oil flowing

gm - gram

GOR - Gas Oil Ratio

I - de Haan's scaling factor

IOIP - initial oil in place

K,k - permeability

kw - permeability in water

ko - permeability to oil

L - length

ml - millilitre

"N" - natural crude oil

N - oil produced

 ΔN_p - increment of oil produced

△P - pressure drop

ΔPi - initial pressure drop

PPM - parts per million

P.V. - pore volume

Swa - average water saturation

S_{wc} - critical water saturation

Swd - downstream water saturation

Swi - irreducable connate water saturation

 $U_{\rm O}$ - oil viscosity

U_w - water viscosity

V - superficial velocity

W_i - water injected

WOR * water oil ratio

W_p - water produced

WP - increment of water produced

5 - interfacial tension

e - contact angle

SCF - standard cubic feet (14.65 psia & 60°F)

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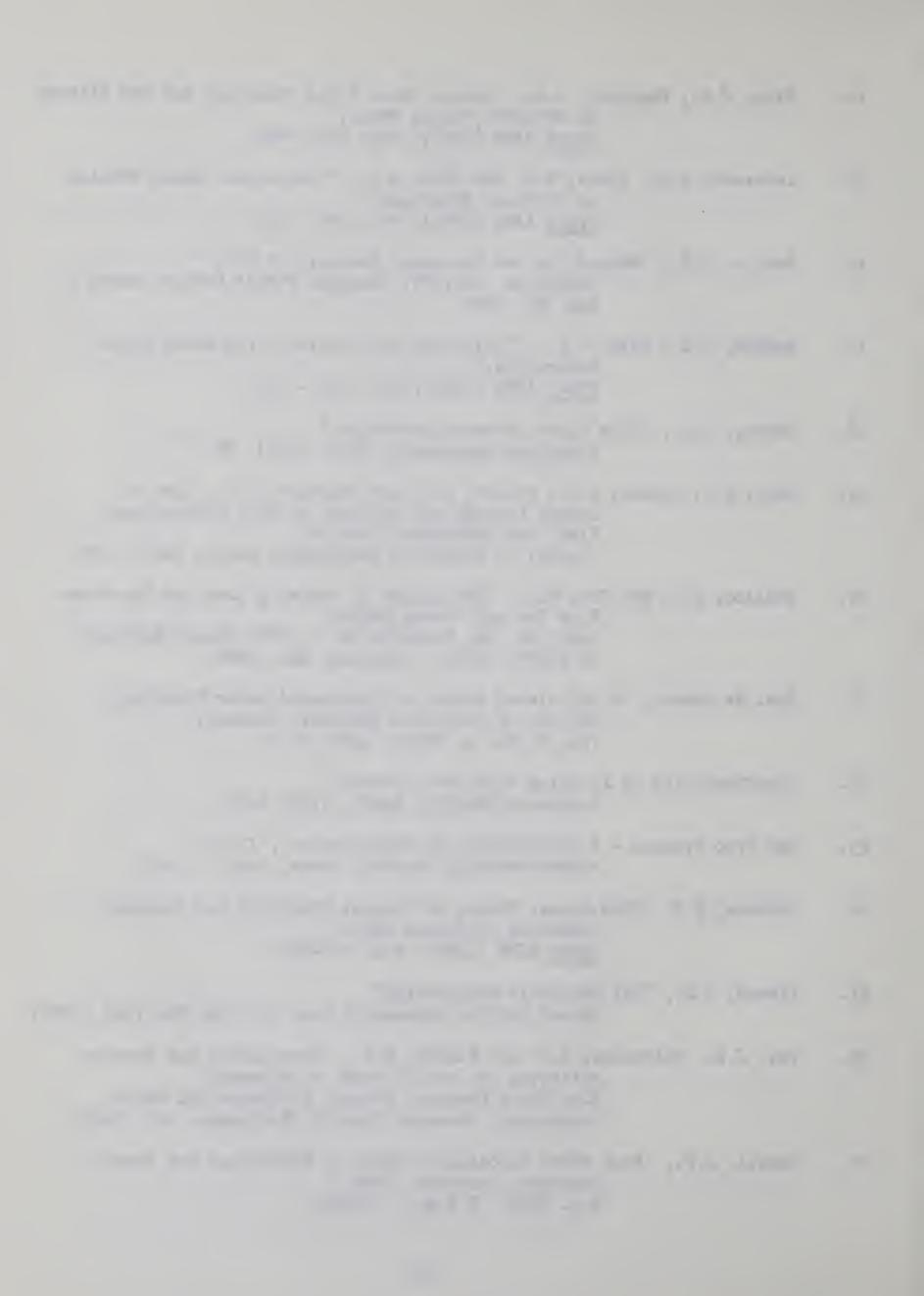
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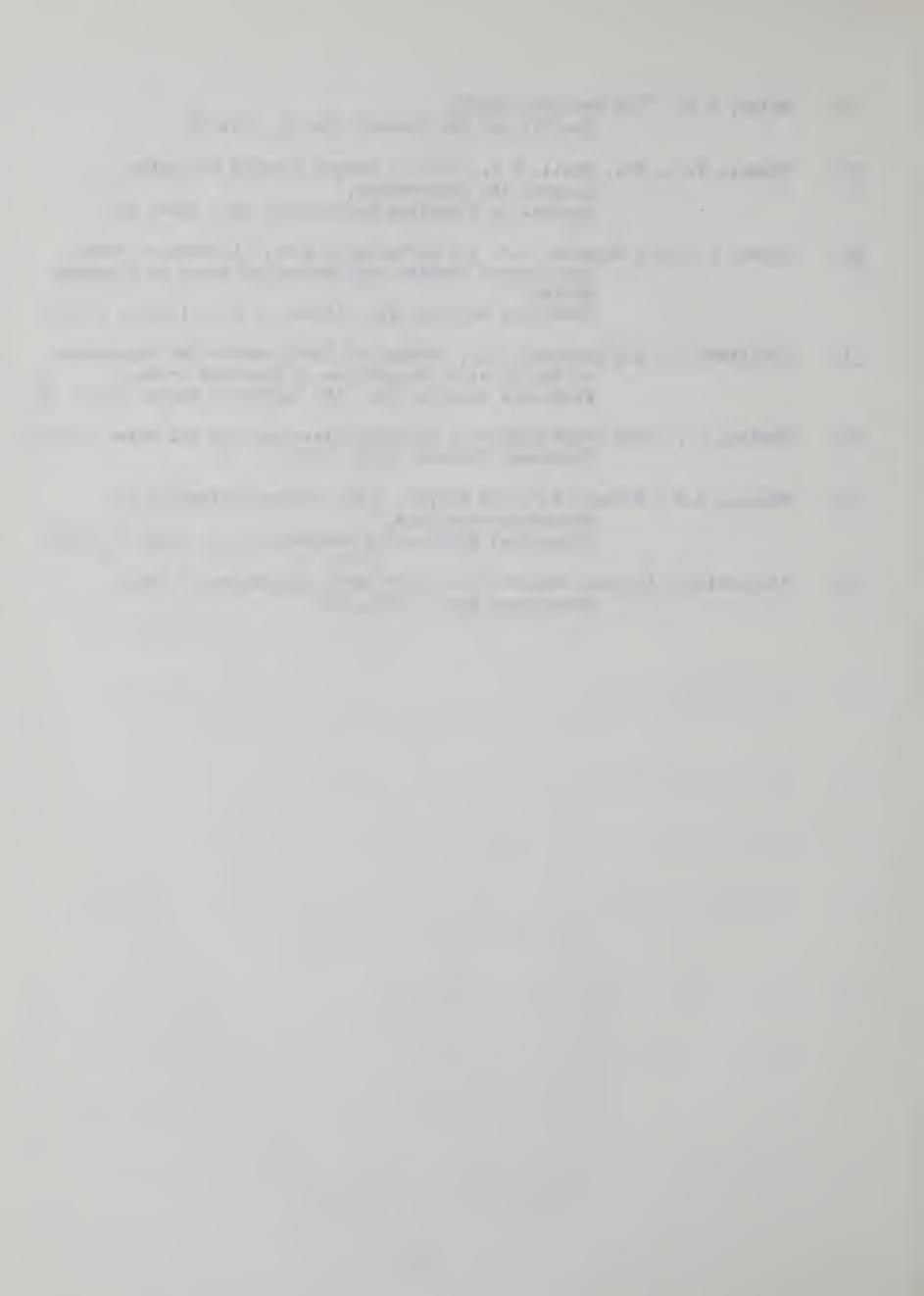
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APPENDIX A

BASIC DATA



TABLE A-1

CORE SAND SAMPLE PROPERTIES

Composit sample from 2008' to 2019' used for core packing

SPARKY SAND - FARGO HUSKY LONE ROCK A - 7

U.S. Mesh	Aparture Diameter Inches	Weight Percent Retained
60	0.0098	4.991
100	0.0059	15.900
150	0.0041	38.381
200	0.0029	31.842
270	0.0021	5.445
325	0.0017	1.455
400	0.0015	0.527
-400		0.539

APPENDIX B

DISPLACEMENT TESTS



DISPLACEMENT TEST RECOVERY DATA - TEST NUMBER 1

80°F t Rate - 10cc/hr in Place - 841.0 c.c.	E OIL	IOIP	0.158	0.207	0.241	0.265	0.285	0.302	0.316	0.326
	CUMULATIVE OIL	P.V. IOIP	441.0	0.188	0.219	0.241	0.259	0.274	0.287	0.296
		AVG. WOR	0.729	976.4	7.137	9.500	12.529	16.000	20.174	24.111
		Wp c.c.	0.79	301.0	508.0	0.869	911.0	1,135.0	1,367.0	1,584.0
	RECOVERY	∆ Wp c.c.	0.79	204.0	207.0	190.0	213.0	224.0	232.0	217.0
	REC	NP c.c.	133.0	174.0	203.0	223.0	240.0	254.0	265.5	274.5
Pore Volume - 926 c.c. Injected Phase - Natural Brine Swi - 0.092		ANp c.c.	133.0	41.0	29.0	20.0	17.0	14.0	11.5	0.6
	CTED	Wi P.V.	0.247	905.0	092.0	0.985	1.233	1.487	1.748	1.992
Pore Volume - Sinjected Phase	BRINE INJECTED	M L C · C	229	6911	407	913	1,142	1,378	1,620	1,846

* Oil viscosity is pressure sensitive.

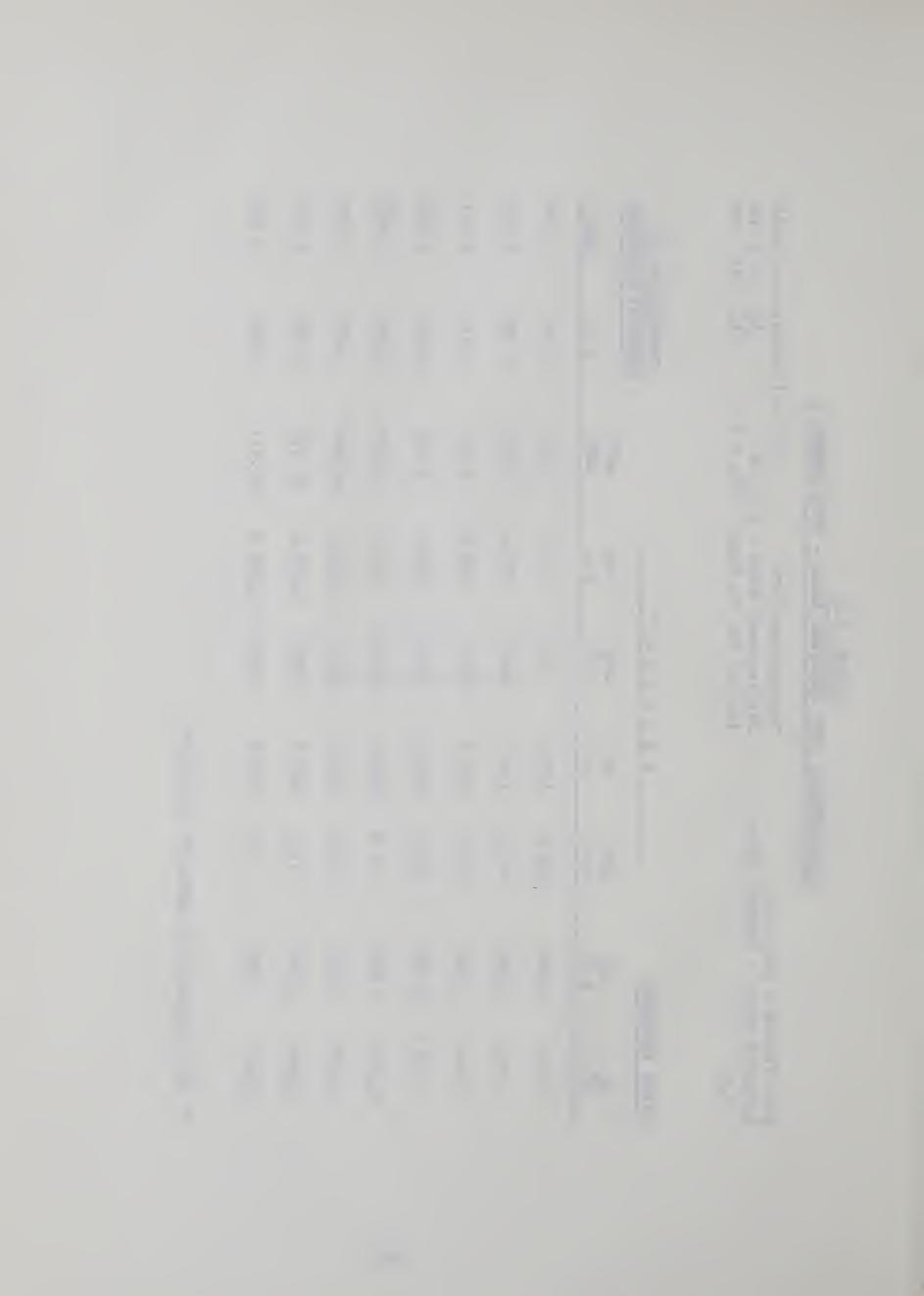


TABLE B-2
DISPLACEMENT TEST RECOVERY DATA - TEST NUMBER 2

- Lloy	$M_{\rm W}=1.03~{\rm cps}$	$^*U_0 = 1220 \text{ cps}$	
Temperature 80°F	(350 psia)	Displacement Rate - 10cc/hr	Initial Oil in Place - 791.5 c.c.
Pore Volume 926 c.c.	Injected Phase - Carbonated Brine	CO ₂ SFC/BBL - BRINE - 62	S _{wi} - 0.146

E OIL	RACTION IOIP	0.169	0.221	0.259	0.290	0.318	0.344	0.369	0.392
CUMULATIVE OIL	P.V. IOIP	0.145	0.189	0.221	0.248	0.272	0.294	0.315	0.335
**	AVG. WOR	0.761	5.409	7.117	8.592	9.489	10.512	11.359	12.278
	M MD O°O	102.0	309.0	522.5	733.0	946.5	1,162.0	1,383.5	1,604.5
ECOVERY	QWp c.c.	102.0	207.0	213.5	210.5	213.5	215.5	221.5	221.0
RECO	Np C. C.	134.0	175.0	205.0	229.5	252.0	272.5	292.0	310.0
	ANp C. C.	134.0	1,1,0	30.0	24.5	22.5	20.5	19.5	18.0
CTED	W W	0.264	0.519	0.788	1.040	1.295	1.549	1.805	2.065
BRINE INJECTED	ĭ ĭ Y	236.0	1485.0	729.0	962.0	1,197.0	1,432.0	1,672.0	1,910.0

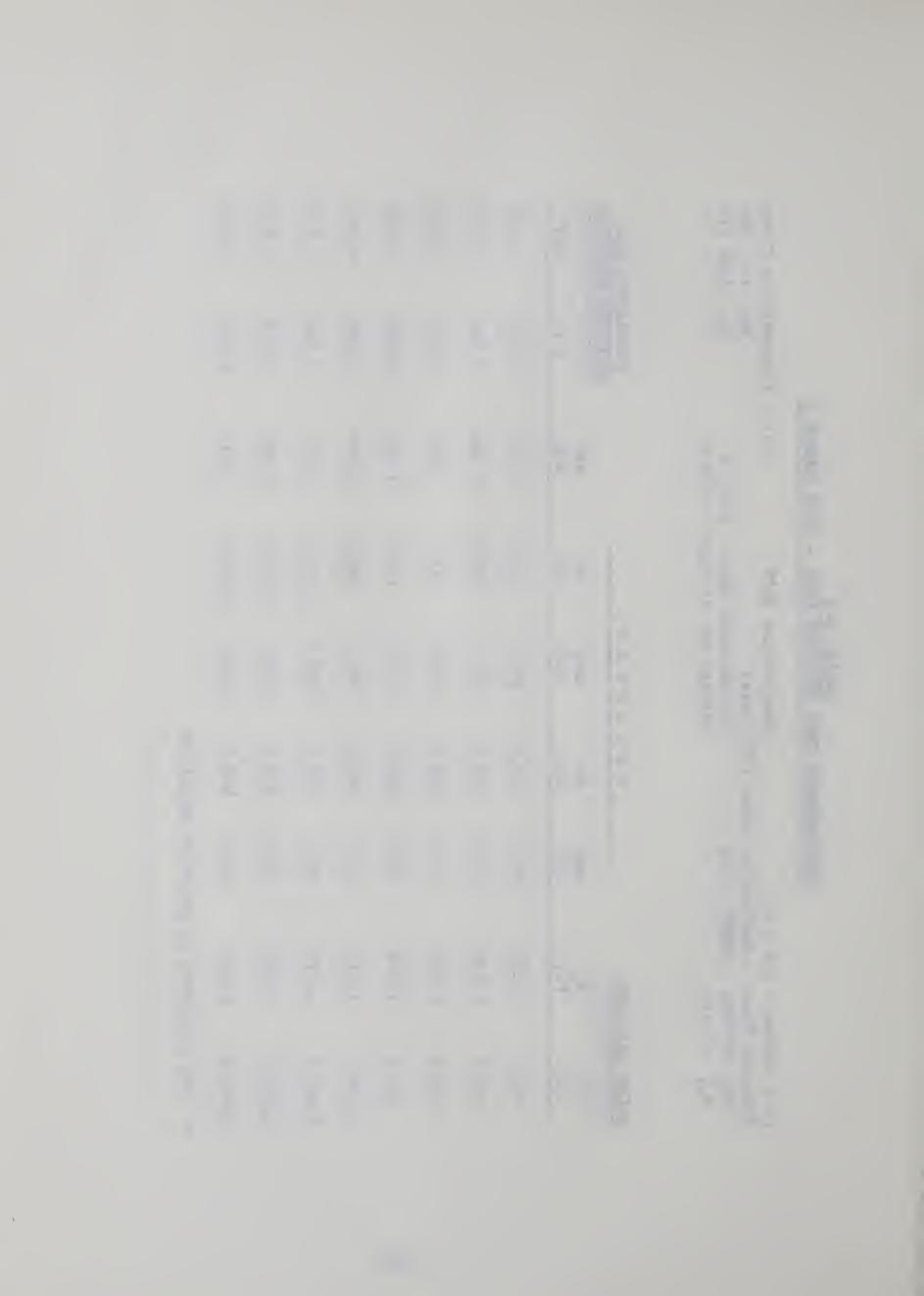
* Oil viscosity is pressure sensitive.

DISPLACEMENT TEST RECOVERY DATA - TEST NUMBER 3

- Lloydminster Crude A. =1.03 cps	=1290
011	/hr 26.50
Temperature 80°F (580 psia)	Displacement Rate - 10cc/hr Initial Oil in Place - 726.
Pore Volume - 926 c.c. Injected Phase - Carbonated Brine	CO ₂ SCF/BBL - BRINE - 101 Swi - 0.217

/E OIL	TOIL	0.198	0.263	0.319	0.367	0.418	0.470	0.514	0.554
CUMULATIVE OIL	, V. q	0.155	0.206	0.250	0.288	0.328	0.369	0.403	0.434
	AVG. WOR	0.729	14.340	5.000	5.956	5.594	5.447	6.328	7.414
	M O O	105.0	209.0	514.0	719.5	926.5	1,133.5	1,336.0	1,551.0
ECOVERY	dwp c.c.	105.0	204.0	205.0	205.5	207.0	207.0	202.5	215.0
RECO	Np c.c.	0°44T	191.0	232.0	266.5	303.5	341.5	373.5	402.5
	o.c.	14400	0.74	41.0	34.5	37.0	38.0	32.0	29.0
CTED	N M.	0.268	0.530	0.792	1.048	1,312	1.577	1.830	2.093
BRINE INJECTED	W ₁ ,	248.0	491.0	734.0	971.0	1,216.0	1,460.0	1,695.0	1,940.0

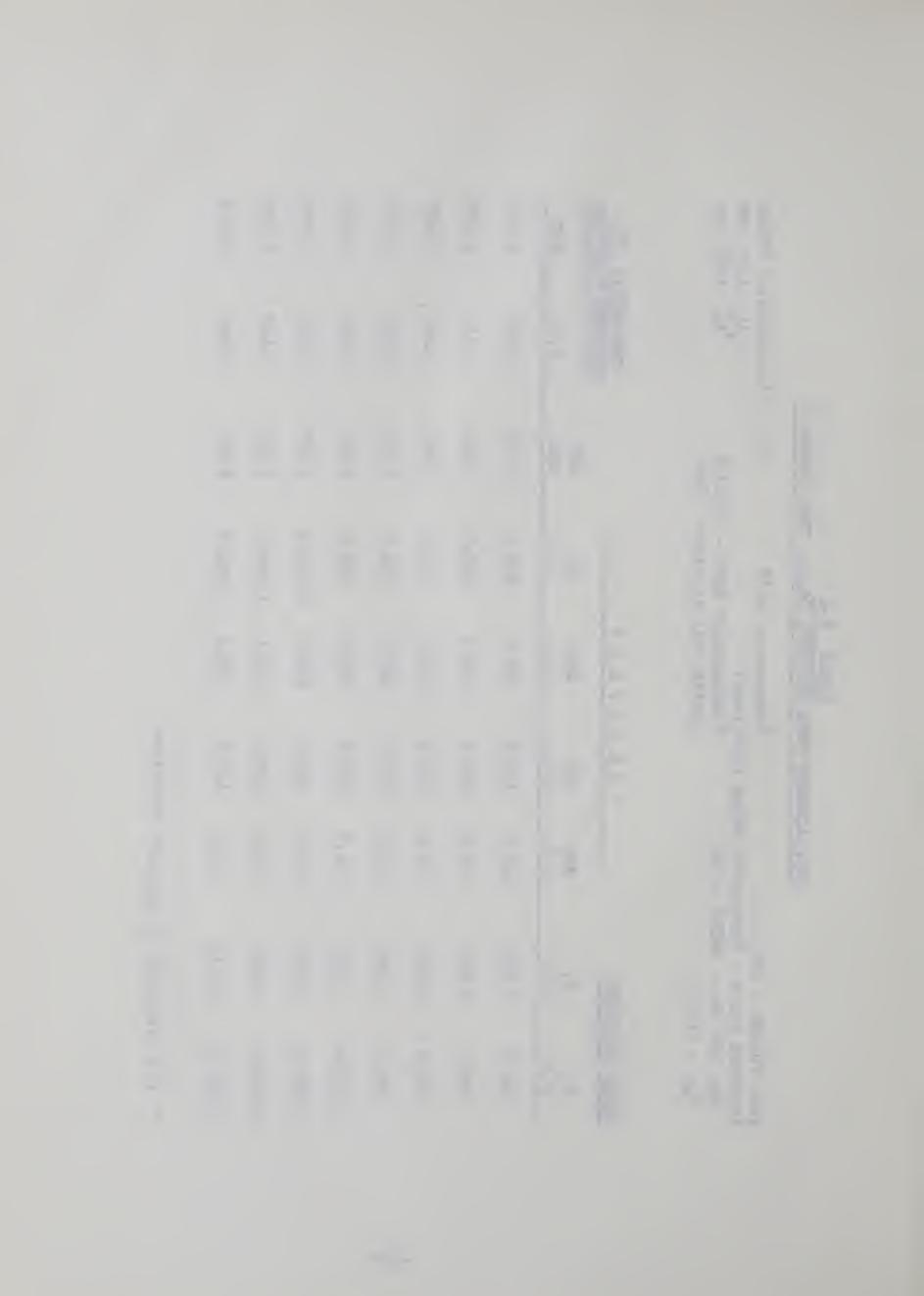
* Oil viscosity is pressure sensitive.



DISPLACEMENT TEST RECOVERY DATA - TEST NUMBER $^{+}$

Pore Volume - 926 c.c. Temperature 80°F 0il - Lloydminster Crude Injected Phase - Carbonated Brine (720 psia) $ \frac{J_W}{S_{\rm wi}} = 1.03 \text{ cps} $ $ S_{\rm wi} = 0.357 $ Initial Oil in Place - 596 Initial Oil in Place - 596	E OIL	IOIP	0.243	0.326	0.405	294.0	0.536	909.0	0.665	0.714
	CUMULATIVE OIL	P.V.	0.157	0.210	0.261	0.301	0.345	0.390	0.428	0.459
		AVG	0.717	4.030	4.489	5.459	5.098	2.000	5.857	6.827
		Wp	104.0	303.5	514.5	716.5	925.5	1,135.5	1,340.5	1,538.5
	OVERY	ΔWp c.c.	104.0	199.5	211.0	202.0	209.0	210.0	205.0	198.0
	REC	Np c.c.	145.0	194.5	241.5	278.5	319.5	3615.	396.5	425.5
		AND c.c.	145.0	49.5	0°24	37.0	77.0	42.0	35.0	29.0
	CTED	Wî. P.V.	0.268	0.531	0.811	1.065	1.337	1.620	1.865	2.113
Pore Volume - Injected Phas CO ₂ SCF/BBL S _{wi} - 0.357	BRINE INJECTED	M L C . C	248.0	1,93.0	0.647	0.486	1,233.0	1,587.0	1,729.0	1,957.0

* Oil viscosity is pressure sensitive



DISPLACEMENT TEST RECOVERY DATA - TEST NUMBER 5

- Lloydminster Crude $\mathcal{M}_{\rm W}$ =1.03 cps $^*\mathcal{M}_{\rm O}$ =1360 cps	
0cc/hr - 542.5	
Temperature 80°F (890 psia) Displacement Rate - 10cc/hr Initial Oil in Place - 542.	
Pore Volume - 926 c.c. Injected Phase - Carbonated Brine CO ₂ SCF/BBL - BRINE - 136 S _{wi} - 0.414	

TE OIL	IOIP	0.267	0.370	0.457	0.536	0.616	0.714	062.0	0.865
CUMULATIVE OIL	P.V.	0.157	0.216	0.268	0.314	0.361	0.418	0.462	0.507
	AVG. WOR	689°0	3.418	4.263	4.697	7, 402	٥٥٥٠ ل	4.829	5.122
	WP C.C.	100.0	288.0	490.5	692.5	0.488	1,096.0	1,294.0	1,504.0
ECOVERY	∆ Wp c.c.	100.0	188.0	202.5	202.0	191.5	212.0	198.0	210.0
REC	Np c.c.	145.0	200.5	248.0	291.0	334.5	387.5	428.5	469.5
	ANp c.c.	145.0	55.5	47.5	43.0	43.5	53.0	41.0	1,100
CTED	W ₁ P,V	0.264	0.521	062.0	1.050	1.303	1.584	1.845	2.120
BRINE INJECTED	W, C,C	245.0	482.0	730.0	972.0	1,207.0	1,468.0	1,710.0	1,963.0

* Oil viscosity is pressure sensitive

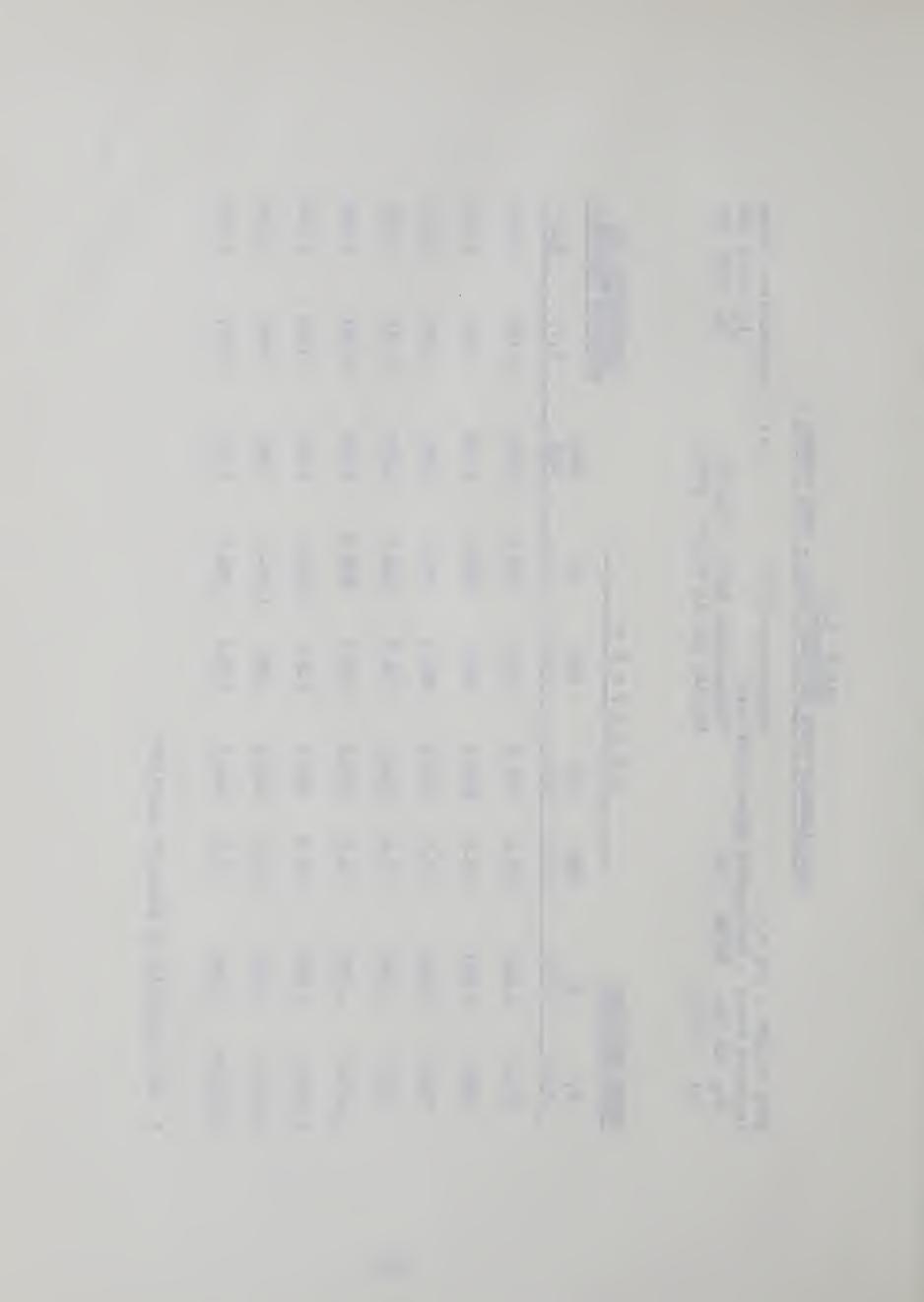


TABLE B-6 RELATIVE PERMEABILITY SAMPLE CALCULATIONS UNSTEADY STATE METHOD OF WELGE

Using Leverett's fractional flow fromula and neglecting capillary pressure and gravity terms

$$f_{W} = \frac{1}{1 + \frac{k_{O}}{k_{W}} \frac{U_{W}}{U_{O}}}$$

$$rewriting \qquad \frac{k_{W}}{k_{O}} = \frac{U_{W}}{U_{O}} \quad \left(\frac{f_{W}}{1 - f_{W}}\right)$$

where
$$f_W + f_O = 1$$

$$WOR = \Delta W_p$$

$$\Delta N_p$$

$$f_O = \Delta N_p$$

$$\Delta N_p + \Delta W_p$$

$$= \frac{1}{1 + WOR}$$

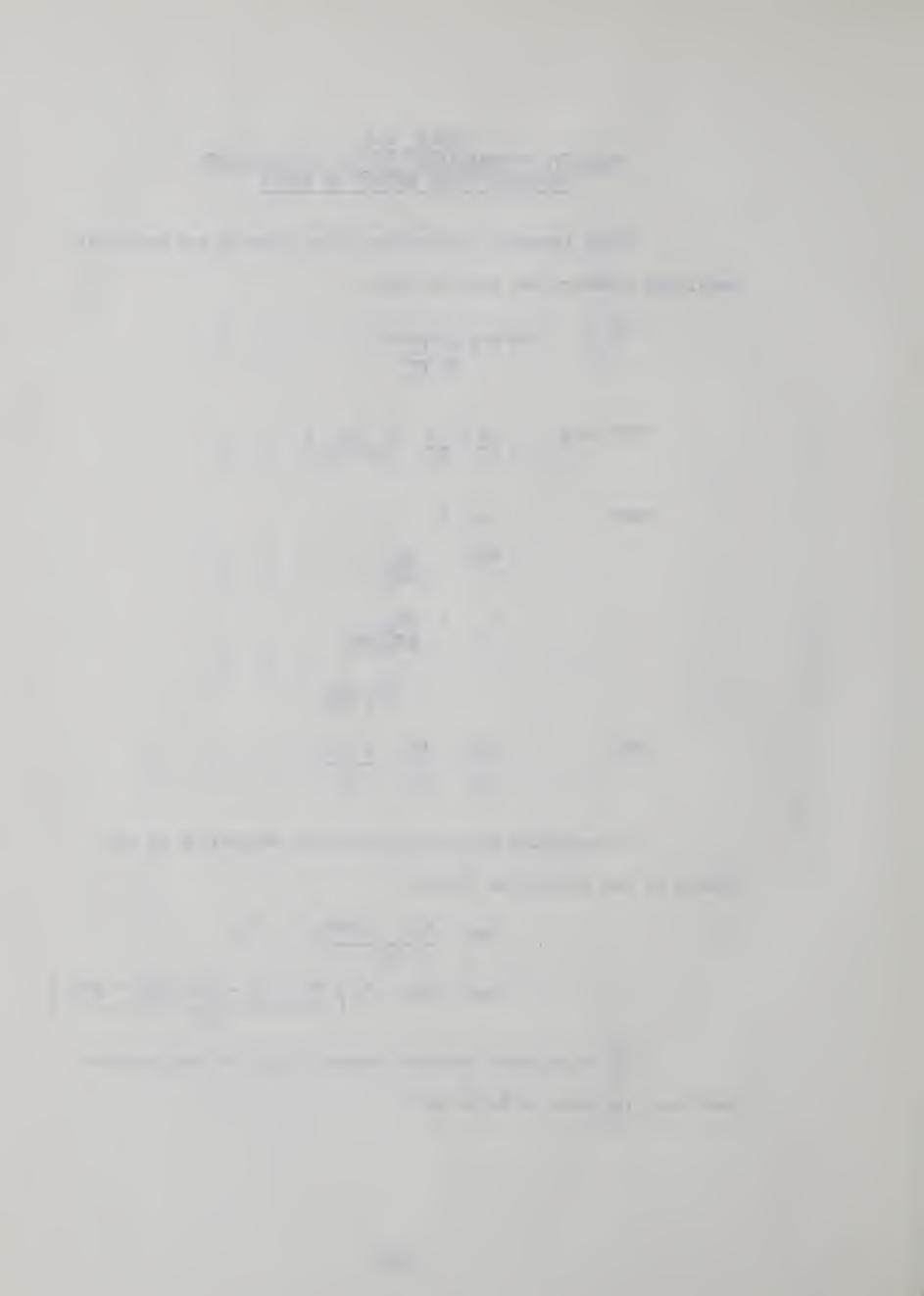
then $\frac{k_{W}}{k_{O}} = \underbrace{\mathcal{U}_{W}}_{O} \quad \frac{1 - f_{O}}{f_{O}}$

To calculate the downstream water saturation at the middle of the production interval

$$S_{wa} = \frac{W_{p} - 1/2\Delta N_{p}}{PV} + S_{wc}$$

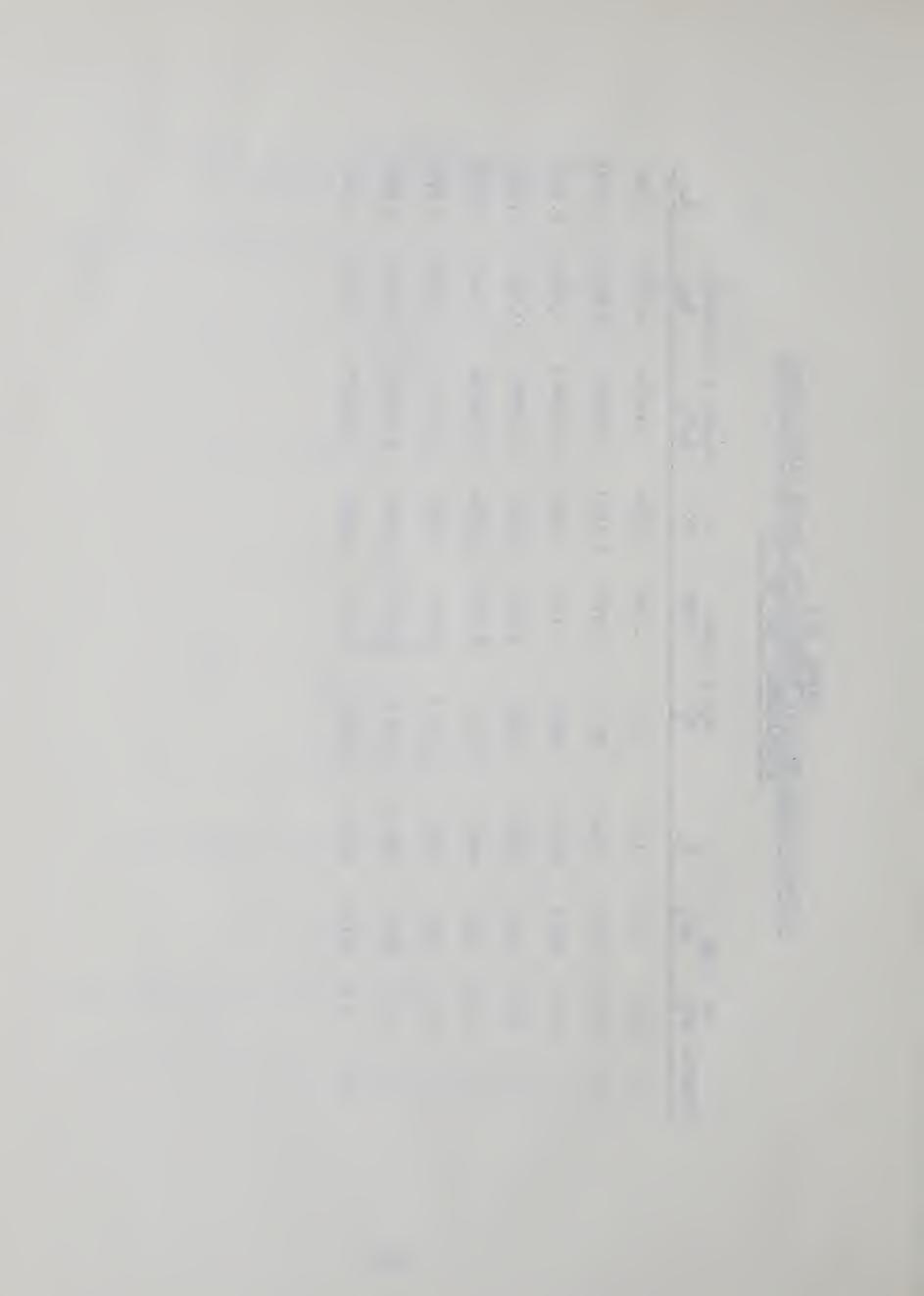
$$S_{wd} = S_{wa} - f_{o} \left(\frac{W_{p} + N_{p} - 1/2 (\Delta N_{p} + \Delta W_{p})}{PV} \right)$$

The calculated relative permeability for displacement test No-1 is shown in Table B-7.



UNSTEADY STATE RELATIVE PERMEABILITY SAMPLE CALCULATIONS
DISPLACEMENT TEST NO - 1

S _W d	0.092	0,1941	0.2167	0,2381	0.2593	0,2780	0.2954	0.3084
3008446 Swa	0.1638	0.2577	0.2955	0.3219	0.3419	0.3586	0.3724	0.3834
$U_{\rm W}/U_{\rm O} = 0.0008446$ $K_{\rm W}/K_{\rm O}$ Swa	919000.0	0.00424	0.006043	0.008027	0.010584	0.013519	0.017050	0.020376
ΓO	0.5784	0.1673	0.1230	0.0952	0.0739	0.0588	0.0472	0.0398
$S_{wi} = 0.092$ W_{p}	. 729	4.976	7.137	9.500	12,529	16,000	20.174	24.111
SW _{V1} W	97.0	301.0	508.0	0.869	911.0	1,135.0	1,376.0	1,584.0
d N	133.0	174.0	203.0	223.0	240.0	254.0	265.5	274.5
926 A Wp	97.0	204.0	. 0.702	190°0	213.0	224.0	232.0	217.0
$PV = 926$ $L \Delta N_{p} \qquad 6$	133.0	41.0	29.0	20°0	17.0	14.0	11.5	0.6
PV INTERVAL Δ N _P	Н	N	8	77	<u>Γ</u>	9	_	∞



APPENDIX - C



TABLE C ANALYSIS OF RESERVOIR WATER

Appearance of Sample = Clear liquid, Small amounts of rust colored sediments.

Components	Mg per litre	Percent of Calculated Solids
Cl	51,467	61.8
co ₃	0	0.0
HCO ₃	118	0.2
SO ₄	2	0.0
ОН	0	0.0
Br	195	0.2
I	12	0.0
Ca	3,540	4.3
Mg	1,681	2.0
Na*(Calc.)	26,243	31.5
Total Solids	83,258	100.0
* Alkali metal:	s calculated as Na	
Density at 60°	र र	1.0583
рH		6.2
H ₂ S		None
Resistivity, ol	nm-meters, 25°C,	0.101
Ref. Index 25°	C	1.3469
Total Solids		
evap. at 110°C		83,470
evap. at 180°C		83,090
after ignition		81,830
Remarks Fe -	some	